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CO-ION TRANSPORT THROUGH ANION EXCHANGE MEMBRANES

by

EDWARD L. CHRISTENSEN

Under the supervision of Professor Walter J. Blaedel

The development of an equation describing the co-ion transport through anion exchange membranes is presented in this thesis. The transport expression is the result of a combination of Fick's First Law of Diffusion with a Freundlich Adsorption Isotherm that describes the partitioning of a co-ion between the external solution and the membrane.

Experimental investigation of the co-ion distribution showed that the ratio of a tracer co-ion in the membrane phase to the solution phase depended upon the bulk co-ion concentration to a fractional power, the value of which in turn depended upon the counter-ion charge type. This was contrary to the behavior predicted by the idealized Donnan Law for co-ions.

Studies on the overall transport of tracer co-ion from one

solution to another separated by an anion exchange membrane were carried out by varying systematically all parameters in the postulated co-ion transport equation, except for the membrane thickness. Good agreement with predicted behavior was found in all cases. The ratio of tracer co-ion in Solution 1 to Solution 2 at any given time was dependent upon the bulk co-ion concentration in Solution 1, raised to the same fractional power found in the distribution investigations.

Distribution and overall transport studies were made in the presence of both univalent and divalent counter-ions, with large differences observed for each charge type. Previous work of this nature had been reported only for univalent counter-ion systems, with no extensive studies made on the divalent species. The data also permitted evaluation of co-ion diffusion coefficients in the membrane, and values were found which were about two orders of magnitude smaller than those in aqueous solutions.
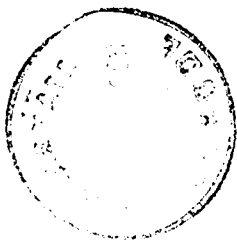
Approved *Walter J. Blaedel*

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A thesis submitted in partial fulfillment of the
requirements for the degree of

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* * * *

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* * * *

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* * * *

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* * * *

To Captain Forrest A. Todd, USN (Retired), who, by his initiative,
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CHAPTER I

INTRODUCTION

DEFINITION OF THE ION EXCHANGE SYSTEM

Any ion exchange system may be characterized by three chemical components. These are the ion exchanger itself, an electrolyte composed of a counter-ion and a co-ion, and a solvent, usually water.

The ion exchanger may be of an almost infinite variety of substances. The first scientifically reported ion exchanger was observed in 1850 by Thompson (49) and Way (51). They reported that equivalent amounts of ammonium and calcium ions could be exchanged by clay. Soon after these English agricultural chemists made their discovery, many other naturally occurring ion exchangers were reported. Among these were the silicate minerals. Leucite, for example, a potassium aluminum silicate, was convertible to analcite, a sodium aluminum silicate, by passing a solution of sodium chloride through the leucite. The reverse reaction was also attainable. Since those early days, widely varying substances such as coal, glass, cellophane, cell membranes, zeolites, and other materials have been used as ion exchangers.

It remained until 1935 for two more English chemists, Adams and Holmes (1), to synthesize an artificial ion exchange resin. This resin consisted of a phenol-formaldehyde condensation polymer which

contained ionogenic groups. These ionic groups were electrostati-
cally neutralized by either a hydrogen ion or a metal ion. De-
pending upon the relative concentrations and strengths of attraction,
one ion could be replaced by another. The importance of this develop-
ment was the fact that the exchange capacity of a given ion exchanger
was now well defined. One equivalent of ion exchanger would react
with one equivalent of ions from the external solution. Most ion
exchangers used previous to 1935 were natural products and the ex-
change capacity of them, though perhaps known, was ill-defined.

Modern ion exchangers may be used in a variety of physical
forms, including spherical beads, discs, plugs, and membranes.
All these, if of the same resin material, exhibit very similar
chemical properties, and each form has its particular advantages
and disadvantages.

The ion electrostatically bound to the ion exchanger is re-
ferred to as the counter-ion. If the exchanger being used has
ionogenic groups having positive charges, for example, quaternary
ammonium groups, then the counter-ion is of the opposite charge, or
negative in this case. Since an ion exchanger must be electrostati-
cally neutral, there is always a counter-ion associated with each
exchange group. However, other counter-ions from an external
solution in contact with the ion exchanger are free to enter the
resin matrix and to exchange with the counter-ion already present.
No electrostatic repulsion is experienced. For example, chloride

ion may enter an anion exchange resin and replace hydroxyl ion
as follows:

$$Cl^- + \overline{OH^-} \rightleftharpoons \overline{Cl^-} + OH^- \qquad (1.1)$$
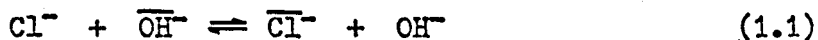
In Equation 1.1 the barred quantities refer to the resin phase.

Since no ion can exist in solution without the presence of
an ion of the opposite charge, a co-ion is also needed to char-
acterize the ion exchange system. This ion has a charge opposite
in sign of that of the counter-ion, being of the same charge as that
of the ion exchanger group itself. In the anion exchange example
referred to above, a typical co-ion would be sodium ion. Since the
co-ion and the ion exchange resin have the same charge type, the
co-ion is electrostatically repelled from the resin matrix and
thus is effectively excluded from the matrix. Co-ions do not ex-
change like counter-ions.

The last chemical component to be considered in an ion ex-
change system is the solvent. This is usually water, although other
solvents have been studied. There is solvent within the resin phase
itself, the amount of which depends upon the nature of the ion ex-
changer and various physical parameters such as temperature and
pressure. In 1951 Gregor (21) defined the role of the solvent by
stating that the ion exchange resin was actually a restrained and
highly concentrated solution of ion exchanger.

OBJECTIVES

Co-ions and counter-ions are transported through an ion ex-change membrane at greatly different rates, with the counter-ions being much faster. The work presented in this thesis is a study of the transport of the co-ion, that ion excluded from the resin matrix, from one solution to another through an ion exchange membrane. The development of equations based on the Nernst-Planck flux theory are presented to characterize the co-ion transport, and experimental evidence supporting these expressions is given.

Previous treatments of co-ion transport through ion exchange membranes were based on the well known Donnan theory and the Nernst-Planck flux equations. However, the resulting equations inadequately described the observed rates of co-ion transport. Early work in this laboratory indicated the need to find the equilibrium distribution of the co-ion between the two phases, external solution and membrane, before the overall transport could be studied. Accordingly, this thesis presents first a description of the co-ion distribution between the membrane and aqueous phases, and then, based on this distribution, a description of the factors upon which the rate of co-ion transport through the membrane depends.

Many applications of ion exchange resins or membranes depend upon exclusion of the co-ion or minimization of its transport, and a knowledge of the factors upon which such exclusion or transport

depends is of great importance. It is hoped that this work will
result in an increased understanding of the co-ion transport through
ion exchange membranes, and of these membranes in general.

LITERATURE SURVEY

Previous work on ion transport and distribution in ion ex-
changers is substantial, although the majority of it deals with
the counter-ion. Most of the work on co-ions has been concerned
with the distribution of the co-ion between the solution and resin
phases, with relatively little work having been done on the overall
transport through the ion exchange membrane. One reason for this
is that synthetic ion exchange membranes are new, having been first
developed in 1953 (33), and with good, thin, and strong membranes
having become commercially available only in the early 1960's.

The Donnan Law

Until about 1961, most of the work done on the co-ion distri-
bution between two phases, external solution and resin, was based
on the membrane equilibrium theory presented by Donnan (13) in 1911.
This theory, presented in modern day terminology by Helfferich (28)
and other workers, states that the activity product of the ions in
solution is proportional to that in the resin phase. For an uni-
univalent electrolyte, AX,

$$a_A a_X = \overline{a}_A \overline{a}_X \qquad (1.2)$$

In the case of an anion exchange resin where A is the co-ion and X is the counter-ion, application of the electroneutrality principle to the solution phase and the membrane phase gives

$$c_A = c_X \qquad (1.3)$$

$$\overline{c}_X = \overline{c}_A + \overline{c}_R \qquad (1.4)$$

The concentration of the exchange groups, R, in the resin phase is $\overline{c}_R$, and is usually approximated as the membrane capacity. This quantity is generally much greater than the co-ion concentration in the membrane, $\overline{c}_A$, and therefore

$$\overline{c}_X \cong \overline{c}_R \qquad (1.5)$$

Substituting Equations 1.3 and 1.5 into Equation 1.2 and replacing activities with concentrations and ionic activity coefficients

$$c_A^2 \gamma_A \gamma_X = \overline{c}_A \overline{c}_R \overline{\gamma}_A \overline{\gamma}_X \qquad (1.6)$$

Solving Equation 1.6 for $\overline{c}_A$,

$$\overline{c}_A = \frac{c_A^2 \, \gamma_A \gamma_X}{\overline{c}_R \, \overline{\gamma}_A \overline{\gamma}_X} \qquad (1.7)$$

Equation 1.7 shows that the co-ion concentration in the resin is directly proportional to the square of the co-ion concentration in the external solution. The combined value of the activity coefficients probably does not differ greatly from unity (see p. 9), and $\overline{C}_R$ is greater than 1.0 $\underline{M}$ for most resins. Therefore, for an external solution concentration of 0.1 $\underline{M}$, $\overline{C}_A$ is 0.01 $\underline{M}$, which is two orders of magnitude smaller than $\overline{C}_X$. In other words, compared to the counter-ion X, the co-ion A is "excluded" from the resin phase.

For the case of any strong electrolyte, A_xX_a, the Donnan co-ion distribution corresponding to Equation 1.7 is

$$\overline{C}_A^x = \frac{a^a C_A^{a+x} \gamma_A^x \gamma_X^a}{\overline{C}_R^a \overline{\gamma}_A^x \overline{\gamma}_X^a} \qquad (1.8)$$

Equation 1.8 reduces to Equation 1.7 for a uni-univalent electrolyte.

Experimental Evaluation of the Donnan Law Co-ion Distribution

Numerous attempts to verify the Donnan Law experimentally have been carried out. In general, the success of these studies has not been good. While a detailed survey of this past work is not intended, a brief look is in order. Work previous to 1939 is well reviewed by Griessbach (25) and will not be considered. Before going further, it must be stated that even though Donnan back in 1911 showed the difference

between co-ions and counter-ions, there are many pieces of work where this distinction is not utilized or only partially used. This has led to a great deal of confusion in much of the early literature.

In 1947, Boyd and coworkers (9) published one of the first papers on the self-diffusion of ions into ion exchangers. However, they were concerned mostly with the counter-ion exchange and had little to say about the behavior of the co-ion.

Gregor (21) in 1951 developed the theory previously mentioned that an ion exchanger could actually be considered as a constrained, concentrated solution of a large polymer containing many ionic groups. Glueckauf (17) in 1952 and others expanded on this theory. Acceptance of these concepts was important because they permitted application of conventional solution principles to the study of the resin phase.

However, the experimental data of many workers did not agree very well with the Donnan theory, and various attempts have been made to modify the equations or to explain the discrepancies. Attempts were made to explain these discrepancies by application of activity coefficients to convert molalities or molarities to activities (3)(11)(12)(20)(23)(24)(26)(27)(31)(34)(35)(37)(41). Experimentally, it appeared that as the external solution concentration of the co-ion went down, the mean molal activity coefficient of the electrolyte within the resin also went down, which is in contrast to normal dilute solution behavior. Some of the above workers explained this anomaly

by invoking increased ion pairing within the resin phase as the external solution concentration decreased.

The importance of the activity coefficients is shown by Equation 1.7. At low external solution concentrations, the behavior of the ionic activity coefficients is well known for many electrolytes, and they approach unity at infinite dilution. The behavior of the resin phase activity coefficients is not well known and they seem to be highly dependent upon crosslinking and swelling. Freeman (15) in 1960 reported that the log of the mean molal activity coefficient varied linearly with the co-ion concentration over a wide range. Glueckauf (19) in 1962 argued that at external solution concentrations of 0.1 $\underline{M}$ or less, the counter-ion concentration within the membrane remained effectively constant since $\bar{a}_A \ll \bar{a}_R$ and therefore, the activity coefficient, whatever it was, should also remain essentially constant. Finally, Freeman (16) in 1965, using new and improved experimental techniques, showed that the mean molal activity coefficient did indeed remain almost constant over the range 0.002 to 0.26 $\underline{M}$.

Freeman (15) has summarized the ion exchange resin uptake of electrolytes from aqueous solutions. Using both original data and that of other investigators, he first described the uptake behavior in general, and then theorized on the deviation of the observed uptake from that which was predicted. The lack of agreement between experiment and theory, once activity coefficient corrections were applied,

was postulated to be due to the presence in the resin of ion exchange groups of a charge type opposite those nominally present. This would lead to the higher than predicted co-ion concentrations in the resin phase, especially at the lower external solution levels. Kraus and Moore (34) had earlier stated that this factor did indeed occur with some ion exchangers, but Freeman pointed out other errors in their work which made their conclusions invalid.

Some workers questioned the validity of the early co-ion distribution experiments, stating that the external solution adhering to the ion exchange resin was responsible for the apparently high co-ion concentration within the resin. Freeman (15), Kraus and Moore (34), and Mackay and Meares (37) were among these. Kraus and Moore used a correction factor for the effect of the retained external solution, but had little success. In 1962 Glueckauf and coworkers (10)(18)(19) described a procedure that corrected for adhering external solution, by measuring the release of the co-ion from an ion exchange membrane as a function of time and then extrapolating back to time zero in order to obtain the "true" membrane co-ion concentration. They did not, however, achieve a linear extrapolation for all the membranes studied.

Solvent transfer and electroosmosis were considered by Oda and Yawataya (42) to affect the co-ion concentrations in an ion exchange membrane, but they did not arrive at a definitive co-ion distribution between the two phases.

Other Co-ion Distributions

It remained until 1962 for someone to break away from the Donnan theory. Glueckauf and coworkers (10)(18)(19) postulated that the resin co-ion concentration was related to the bulk electrolyte concentration, but differently from the Donnan relationship of Equation 1.7.

$$\bar{c}_A = kc_X^{2-z} \tag{1.9}$$

The exponent 2-z was found to be about 1.3 for systems with 1:1 electrolytes, definitely different from the value of 2 required by the Donnan theory. They then concluded that since the Donnan Law must apply to a pair of homogeneous phases, the resin phase must be heterogeneous. Based on this heterogeneity, they then developed rather complicated expressions for co-ion uptake and transport.

Theories of ion exchange and co-ion behavior have been postulated in the past other than the Donnan Law. These include the controversial Teorell-Meyer-Sievers theory (38)(39)(40)(48), the McMillan-Mayer treatment (30)(47), and others. Some of these have been discarded on the basis of present day knowledge, while others are extremely complicated and difficult to work with quantitatively. An excellent review by Lakshiminarayanaiah (36) on ion exchange membranes covers the majority of the work in this field from 1955 to 1965.

CHAPTER II

CHARACTERIZATION OF THE AMF ANION EXCHANGE MEMBRANE

The ion exchange membrane used in this work was an AMF A-104-EB anion exchange membrane manufactured by the American Machine and Foundry Company, Springdale, Conn. This type of membrane is prepared by the impregnation of a film of polyethylene with small particles of polystyrene, followed by exposure to ^{60}Co gamma radiation, which causes grafting of the polystyrene to the polyethylene backbone. After grafting, the film is subjected to chloromethylation followed by amination with a tertiary amine, in order to introduce one quaternary ammonium group per polystyrene unit. A quasi-homogeneous membrane results, which contains strong anion exchange groups. The homogeneity of the membrane depends upon the uniformity of the polystyrene impregnation and upon the effectiveness of the grafting procedure. The grafted membranes are thinner, stronger, and much more homogeneous than those prepared earlier by imbedding particles of ion exchange resin in an inert binder such as collodion.

According to the manufacturers' specifications, the membrane has a nominal wet thickness of 6 mils (0.015 cm), an ion exchange capacity of 1.5 meq per gram of dry membrane, a water content of 20% on a dry basis, and a Mullen burst strength (wet) of 50 psig (2). Other authors (10) have shown the membrane to have a water content of 11% on a wet basis. The membrane properties of capacity, density, and wet thickness

were investigated and measured independently in this laboratory, because an accurate knowledge of these properties is necessary for the theoretical interpretation of the distribution and transport measurements. Methods used to measure these properties are described in some detail in this chapter because they represent some improvement over presently used procedures.

MEMBRANE CAPACITY

A determination of the membrane capacity is necessary since the co-ion exclusion and the point at which it breaks down is dependent upon the capacity (Equation 1.7). Even though the determination of the membrane capacity is a straightforward procedure, the expression of the results is not. A wide variety of capacity expressions exist, including capacities expressed as meq/g of dry resin, meq/g of wet resin, and meq/g of swollen water. Helfferich (28) in his treatise on ion exchange lists eight different types of capacities, most of which may be interrelated. The use of so many varieties, however, can lead to confusion. In this work, the membrane capacity will be expressed in meq/cm^3 of resin in the wet form, primarily because this quantity is most closely related to the molarities used to express homogeneous solution concentrations.

In order to measure the capacity of the anion exchange membrane, the membrane was converted to the chloride form by equilibration with 1.00, 0.10, or 0.01 $\underline{M}$ NaCl solutions. The membrane was then blotted

dry and weighed. It was next placed in water for one hour to leach out the chloride within the membrane that was not actually held by an ion exchange group. Without such leaching, capacities that were several percent higher were obtained. The leaching with water does not affect the chloride attached to an ion exchange group, because the chloride counter-ion cannot be replaced by pure water.

The water leaching was followed by a 24-hour immersion in 50 ml of 4% Na_2SO_4. This concentration was high enough, and sulfate was held strongly enough by the membrane to extract all of the chloride. The membrane was removed from the extractant solution and rinsed, the rinsings being added to the extract. Water was then added to the solution to make a total volume of 100.0 ml.

Duplicate aliquots of the chloride extract were titrated for chloride by the Volhard procedure (8). The appropriate calculations were then made in order to find the milliequivalents of chloride displaced from the membrane. By knowledge of the membrane weight and density (see following section), the volume of the membrane was determined. The combination of these data gives the ion exchange capacity in meq/cm^3 of membrane. Capacities were measured for the membrane in equilibrium with NaCl at three concentrations - 1.00, 0.10, and 0.01 M. The capacity at each concentration is the average of three determinations, with duplicate titrations for each. The titrations checked well within the 1% level, and the standard deviation of the triplicate determinations was about 2.0%. Results

are summarized in Table 2.1.

Table 2.1 shows the membrane capacity to be 1.048 meq/cm^3 for equilibrating solutions of 0.10 and 0.01 $\underline{M}$ NaCl. At 1.00 $\underline{M}$ NaCl the apparent capacity is about 8% higher. It is believed that this high value is due to the increased NaCl penetration of the membrane at high external solution concentrations. Since the systems studied seldom contained electrolyte at concentrations higher than 0.10 $\underline{M}$, the membrane capacity was taken to be 1.048 meq/cm^3 for all purposes.

An attempt was made to check this capacity by conversion of the membrane to the hydroxide form, and then to titrate it with a standard HCl solution, following the neutralization reaction with a pH meter. The procedure used was as follows. The membrane was converted to the hydroxide form by repeated equilibration with 0.10 $\underline{M}$ NaOH. It was then weighed and placed in a solution of 0.10 $\underline{M}$ NaCl having a volume one hundred times the membrane volume. After letting the NaCl solution-membrane mixture stand for 24 hours, a pH titration with 0.10 $\underline{M}$ HCl was carried out.

Titrations on several pieces of membrane in the hydroxide form gave titration curves like that shown in Figure 2.1. The capacity of the membrane as determined from this procedure was about 0.5 meq/cm^3, much less than the 1.048 meq/cm^3 found by the Na_2SO_4 method. This low value was attributed to hydrolysis of some of the exchange groups by the NaOH. It was also observed that longer times of equilibration with NaOH before titration resulted in membrane

TABLE 2.1

ANION EXCHANGE MEMBRANE CAPACITY

Equilibrating Solution Concentration, $\underline{M}$	Membrane Capacity meq/cm^3
1.00	1.132
0.10	1.048
0.01	1.049

FIGURE 2.1

pH TITRATION OF THE ANION EXCHANGE MEMBRANE IN THE HYDROXIDE FORM
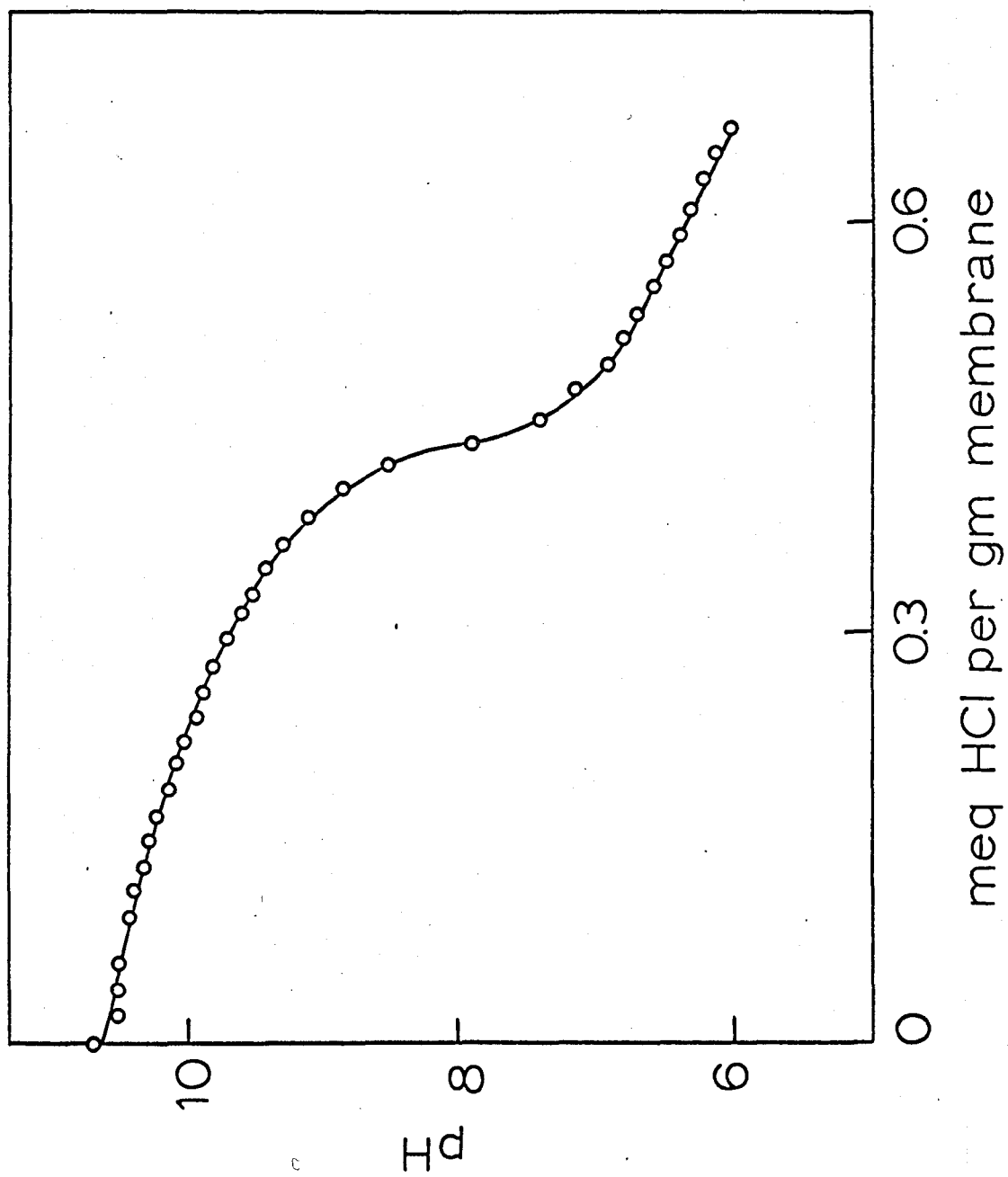
capacities less than 0.5 meq/cm^3. No attempts were made to check further the capacity of 1.048 meq/cm^3 which was assumed to be a strong base capacity.

MEMBRANE DENSITY

The ion exchange membrane density is necessary for two reasons: first, to calculate the volume of a piece of membrane from its known weight for the capacity measurements, and second, to calculate the membrane thickness.

In this study, a pycnometric method was used (44). In practice, a piece of membrane was equilibrated for at least 24 hours with the appropriate electrolyte solution, changing this solution several times to insure that the desired form of the membrane was achieved. After removing the membrane from the solution, surface moisture was blotted from it with tissue. The blotted membrane was then weighed and cut into sections small enough to fit into the pycnometer. The pycnometer was filled with the membrane and a solution identical to that used in the equilibration step, and the total weight was found. Next, the weight of the pycnometer was found filled with the same solution, but without the membrane. These data permitted the calculation of the membrane density.

$$\bar{\rho} = \frac{a\rho}{a + b - c} \qquad (2.1)$$

In Equation 2.1, $\bar{\rho}$ is the membrane density, ρ is the solution density, a is the weight of the membrane, b is the weight of the pycnometer filled with solution only, and c is the weight of the pycnometer filled with solution and membrane.

The data for the ion exchange membrane density, measured at room temperature ($24-28^{\circ}$C) are given in Table 2.2 for a single membrane specimen equilibrated with ten electrolytes, each at two concentration levels, and with water. Each value is an average of three determinations. The average value of the membrane density is 1.020 g/cm^3. The median standard deviation of each set of triplicates is 0.008 g/cm^3, and the standard deviation of all triplicates in Table 2.2 is 0.015 g/cm^3. There are definitely larger differences among the densities in different electrolytes and at different concentrations than can be accounted for by the precision of the triplicate measurements. However, since these differences are only at the 1-2% error level, the average membrane density of 1.020 g/cm^3 was taken as representative for the membrane in all salt solutions having concentrations around 0.10 $\underline{M}$ or less.

MEMBRANE THICKNESS

Direct measurement of the membrane thickness is elusive. Two general methods involve direct measurement with a micrometer (52) and measurement with a microscope of a section of the membrane mounted on a microscope slide (5). The micrometer often gives scattered results

TABLE 2.2

MEMBRANE DENSITY AND THICKNESS

Electrolyte	Concentration $\underline{M}$	Membrane Density, g/cm^3	Membrane Thickness, cm
NaCl	0.10	1.002	0.0151
NaCl	0.01	0.991	0.0159
NaCl*	0.10	1.020	0.0147
NaCl*	0.01	1.014	0.0150
CsCl	0.10	1.018	0.0151
CsCl	0.01	0.990	0.0156
Na_2SO_4	0.10	1.015	0.0163
Na_2SO_4	0.01	1.037	0.0157
Na_2SO_4**	0.10	1.028	0.0153
Na_2SO_4**	0.01	1.031	0.0153
Cs_2SO_4	0.10	1.038	0.0150
Cs_2SO_4	0.01	1.041	0.0153
$BaCl_2$	0.10	1.028	0.0147
$BaCl_2$	0.01	1.014	0.0149
$SrCl_2$	0.10	1.016	0.0153
$SrCl_2$	0.01	1.004	0.0151
$AgNO_3$***	0.10	1.151	0.0161
$AgNO_3$***	0.01	1.151	0.0161
NaOH	0.10	1.034	0.0149
NaOH	0.01	1.028	0.0154
water ****	–	1.027	0.0156
average	–	1.020	0.0153

    *   Contains 10^{-5} $\underline{M}$ CsCl
   **   Contains 10^{-5} $\underline{\underline{M}}$ Cs_2SO_4
  *** $AgNO_3$ reacted with the membrane, forming a dark film on its surface. These data are not included in the averages.
****   Mean of 6 determinations

since the membrane is not rigid, and thus, the thickness read off the
dial is quite dependent upon the tension placed on the tightening
screw. As a result, numerous measurements must be made before a re-
liable thickness is obtained. In the second method, distortion of the
edge by slicing or cutting, or by the adhesive used to mount the speci-
men may cause error. Both methods have an additional disadvantage in
that they measure only a local membrane thickness, which might vary
considerably. All of these problems may be diminished if an average
membrane thickness based on volume and area is calculated.

To avoid these disadvantages, the thickness was therefore found
indirectly, measuring the weight and density as described in the
previous section of a piece of membrane whose area, 11.58 cm^2, was
precisely known. Table 2.2 shows the results of the thickness deter-
minations as a function of both electrolyte and concentration. The
mean thickness is 0.0153 cm. Each value of the membrane thickness
is the average of three determinations, the median standard deviation
of which is 0.0001 cm. The standard deviation of all triplicates is
0.0004 cm.

As with the membrane density, there are definitely larger dif-
ferences among the thicknesses in different electrolytes and at dif-
ferent concentrations than can be accounted for by the precision of
triplicate measurements. However, since these differences are only
at the 2-3% error level, the mean thickness of 0.0153 cm was taken
as representative for the membrane in all salt solutions having con-

centrations of 0.10 $\underline{M}$ or less.

It must be mentioned that the membrane as received varied extensively in thickness from one part of the roll to another. This variation, as measured by the above techniques, ranged from 0.0081 to 0.0163 cm. Variations of such a magnitude were intolerable, and therefore, a portion of the membrane having as uniform a thickness as possible was selected for the measurements of Table 2.2, and for all further studies.

For the actual membrane thickness determination in Table 2.2, a single piece of membrane was employed, equilibrating it to the appropriate solution, making the measurements, and then equilibrating it again to another solution. This eliminated any variation from one piece of membrane to another. Also, even though these experiments required several weeks, no trend in the data due to wearing or chipping was observed.

EXCHANGE AND PERMSELECTIVITY

The exchange capabilities of ion exchangers have been intensively studied in the past. This ability of an ion exchanger to exchange counter-ions reversibly is of fundamental importance. Almost as important is the fact that such exchange must occur at a reasonable rate.

An earlier study co-authored with Blaedel (4) established the exchange characteristics of the A-104-EB anion exchange membrane. In that study, presented in Appendix I, and that by Blaedel and Haupert

(6), it was shown that at ion exchange equilibrium, the following equation describes the compositions of two solutions separated by an ion exchange membrane.

$$\left[\frac{c_{A,1}}{c_{A,2}}\right]^{z_B/z_A} = \frac{c_{B,1}}{c_{B,2}} \qquad (2.2)$$

Here z is the counter-ion charge. This relationship was verified by Blaedel and coworkers for several systems. Though Equation 2.2 holds for all concentrations, all the work in Appendix I and the present study involves B at tracer levels, the B concentrations being much less than those of A. Thus, in any system, the initial concentration ratio of A in the two solutions sets that of B at ion exchange equilibrium, and the equilibrium A concentrations are the same as the initial concentrations.

It is important in understanding permselective ion exchange membranes to realize that two different states of equilibrium exist, and that any real system progresses toward both states concurrently, but at different rates. Figure 2.2 shows both equilibria schematically.

The first case, ion exchange equilibrium, refers to that equilibrium established when the counter-ions have distributed themselves in such a way as to satisfy Equation 2.2. For example, consider that an anion exchange membrane separates two solutions of equal volume

FIGURE 2.2

COMPARISON OF ION EXCHANGE AND CHEMICAL EQUILIBRIUM
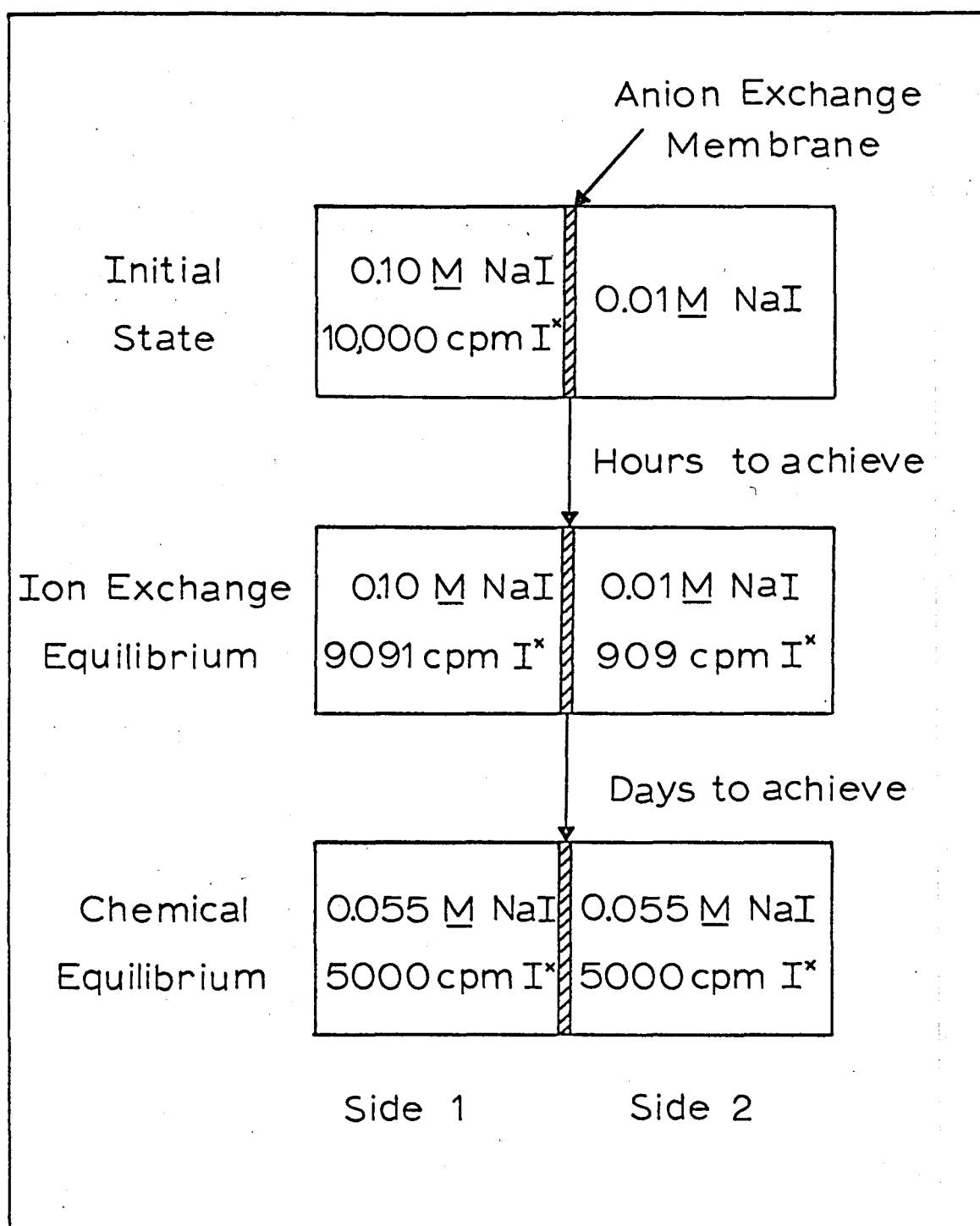
having initial concentrations of 0.10 and 0.01 $\underline{M}$ NaI, respectively.
When a small amount of ^{125}I is added to the 0.10 $\underline{M}$ NaI solution,
the radiotracer iodide ion will distribute itself at counter-ion ex-
change equilibrium between the two solutions in a ratio of 10:1.
For this equilibrium, only counter-ions need to migrate, and about
15 hours are required with moderate stirring.

At chemical equilibrium the concentrations of each species on
both sides of the membrane are equal. In the above example, chemical
equilibrium is reached when the NaI concentration is 0.055 $\underline{M}$ on each
side of the membrane, and when the radiotracer activity is the same
on each side. For this equilibrium, both counter-ions and co-ions must
migrate. Because the co-ion is highly excluded from the resin matrix,
the process of attaining chemical equilibrium takes a long time, of
the order of several days.

Since days are required to reach chemical equilibrium, very
little deviation from the initial concentrations of the bulk electro-
lyte are noticed by the time ion exchange equilibrium is reached. It
is the large scale time difference in reaching these two equilibria that
causes the membrane to be permselective. Qualitatively, permselectivity
defines the ability of the ion exchanger membrane to allow free passage
through it of one charge type of ion, the counter-ion, while restricting
severely the passage of the oppositely charged type of ion, the co-ion.

The anion exchange membrane used in this study is highly perm-
selective. Table 2.3 from Appendix I illustrates the relative transport

TABLE 2.3

RELATIVE TRANSPORT OF ^{125}I AND ^{137}Cs THROUGH ANION EXCHANGE MEMBRANES

Time, hours	Transported, %	
	^{125}I counter-ion	^{137}Cs co-ion
1	27.5	0
2	39.0	0
4	45.3	0.002
8	47.8	0.008
24	48.4	0.032

of two radiotracers, ^{125}I and ^{137}Cs, from a 0.01 $\underline{M}$ NaI solution,

across an anion exchange membrane in the iodide form, into 0.01 $\underline{M}$

NaI on the other side, as a function of time. It is apparent that

the initial rate of ^{125}I counter-ion transport is several orders of

magnitude higher than that of the ^{137}Cs co-ion. Ion exchange equil-

ibrium is practically complete in about eight hours, during which

time the move toward chemical equilibrium has barely begun.

CHAPTER III

THEORY

DESCRIPTION OF THE SOLUTION-MEMBRANE SYSTEM

Counter-ion transport from one solution to another through an
ion exchange membrane has been shown to be limited by three types
of rate processes (7)(36); (1) diffusion through the liquid films
adjacent to the membrane, (2) heterogeneous ion exchange at the
two membrane-solution interfaces, and (3) diffusion through the
membrane itself. With thin, modern membranes, and with efficient
stirring, the half-time of such counter-ion transport is of the
order of minutes (28). In contrast to counter-ions, co-ions are
practically excluded from the membrane, and the co-ion transport
process is much slower. The liquid film diffusion process (shown
to have a half-time of the order of minutes with moderate stirring
(28)) cannot be rate determining in an overall co-ion transport pro-
cess where the half-time is of the order of hours. The heterogeneous
surface exchange reaction in counter-ion transport has no counter-
part in co-ion transport. Hence, the co-ion transport mechanism
is much simpler than counter-ion transport, being describable as
a diffusion process through the ion exchange membrane itself.

The ion exchange membrane-solution system used in this work is
shown in Figure 3.1. In this schematic the membrane is an anion
exchanger and the external solution contains components AX and BX,

FIGURE 3.1

SCHEMATIC REPRESENTATION OF THE ION EXCHANGE MEMBRANE-

EXTERNAL SOLUTION SYSTEM

Solution 1 | Membrane | Solution 2

AX, $C_{A,1}$ $\underline{M}$
BX, $C_{B,1}$ $\underline{M}$

AX, $C_{A,2}$ $\underline{M}$
BX, $C_{B,2}$ $\underline{M}$

$\overline{L}$

$C_{A,1}$ $\overline{C}_{A,1}$ $\overline{C}_{A,2}$ $C_{A,2}$

$C_{B,1}$ $\overline{C}_{B,1}$ $\overline{C}_{B,2}$ $C_{B,2}$

$C_{X,1}$ $\overline{C}_{X,1}$ $\overline{C}_{X,2}$ $C_{X,2}$
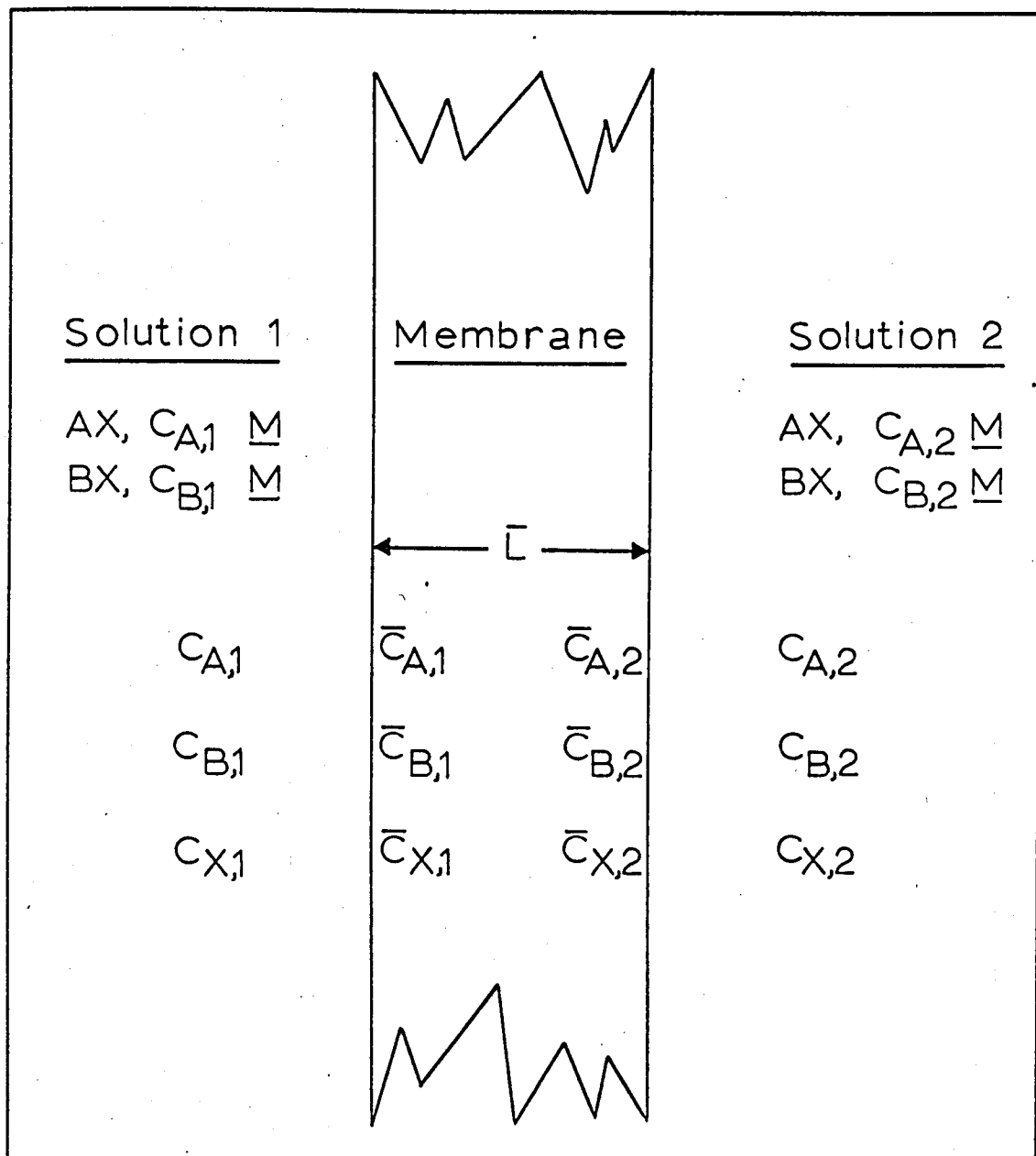
with A and B being the co-ions and X the counter-ion. If the concentration of BX is much smaller than that of AX, then $C_A \cong C_X$ in each solution. Though this simplication is not absolutely necessary, it does greatly simplify the equations. In this work, BX is at tracer levels, 10^{-5} M or less, while AX is always at least 0.001 M in the external solution. Within the membrane phase, denoted by the use of barred quantities, the concentration of X is high, about equal to the capacity of the ion exchange membrane. If the membrane is well equilibrated with X, then $\overline{C}_{X,1} = \overline{C}_{X,2} = \overline{C}_X$, which is the capacity. It is assumed that every ion exchange group has associated with it an X at all times. However, there is also some X within the resin matrix that is not associated with an exchange group, but rather, is associated as AX or BX held by a mechanism other than ion exchange. According to the electroneutrality principles, the X present in the membrane above that needed to satisfy the ion exchange capacity must be accompanied by a co-ion, either A or B.

If the transport through the membrane is assumed to be a simple diffusional process that is describable by Fick's Law, then

$$J_B = -D_B\left[\frac{d\overline{C}_B}{d\overline{L}}\right] \tag{3.1}$$

In Equation 3.1, J_B is the flux of co-ion B, $\overline{D}_B$ is the diffusion coefficient of B within the membrane, $\overline{C}_B$ is the concentration of B in

the membrane, and $\overline{L}$ is the distance through the membrane in which diffusion of B occurs. With only a trace of B in the system, the membrane is essentially in the X form, and its composition is constant throughout. Therefore, $\overline{D}_B$ may also be regarded as constant throughout the membrane. If a linear concentration gradient is assumed for B

$$J_B = \left[\frac{-\overline{D}_B}{\overline{L}}\right](\overline{C}_{B,1} - \overline{C}_{B,2}) \qquad (3.2)$$

Before Equation 3.2 becomes evaluable or useful, it is necessary to relate the membrane concentrations of B to the measurable solution concentrations of B. This requires a knowledge of how B is distributed between the solution and membrane.

DEVELOPMENT OF A SOLUTION-MEMBRANE DISTRIBUTION EXPRESSION FOR CO-IONS

It is well established (28) that the co-ion concentration within the membrane phase is generally much smaller than in the external solution and thus, right at the membrane-solution interface a distribution of A and B must occur. In Chapter I, the simple Donnan Law expression (Equation 1.7) was shown to give an inadequate description of the co-ion distribution.

Two distributions were investigated before one was found that

adequately described the partitioning of a co-ion between the two phases. These were a simple Freundlich Adsorption Isotherm for species B alone, and a theory postulating the presence of small amounts of cat-ion exchange groups in the anion exchange membrane. Both distributions and the resulting co-ion transport equations, counterparts of Equations 3.6 and 3.10, respectively, are shown in Appendix II. In each case the predicted transport of co-ion B showed a dependence upon the bulk elec-trolyte concentration which definitely did not agree with experiment.

The successful distribution expression was found by assuming that the bulk co-ion, A, is distributed between the membrane and solution according to the Freundlich Adsorption Isotherm:

$$\bar{c}_A = kc_A^{(n + 1)} \tag{3.3}$$

Rearranging

$$\frac{\bar{c}_A}{c_A} = kc_A^n \tag{3.4}$$

Next, it was assumed that there is no chemical specificity in co-ion adsorption, in which case there is perfect mixing of the trace B co-ions with the bulk A co-ions:

$$\frac{\overline{C}_A}{C_A} = \frac{\overline{C}_B}{C_B} \qquad (3.5)$$

This relationship is not without precedence in ion exchange studies; Helfferich uses a similar identity in one of his derivations ((28) p. 263). Table 4.2 shows that this identity for trace co-ions Cs and Na in bulk solutions of NaCl and Na_2SO_4 does hold fairly well.

Substituting Equation 3.5 into 3.4, the following expression is obtained.

$$\frac{\overline{C}_B}{C_B} = kC_A^n \qquad (3.6)$$

Or

$$\overline{C}_B = kC_BC_A^n \qquad (3.7)$$

This equation relates the co-ion B concentration in the membrane to the solution concentrations of A and B, and permits Equation 3.2 to be solved.

DERIVATION OF THE EQUATION DESCRIBING CO-ION TRANSPORT ACROSS ION EXCHANGE MEMBRANES

Equation 3.7 may be used to express the B co-ion concentrations in the membrane in terms of the measurable solution components. Thus

$$J_B = \left[\frac{-\overline{D}_B k}{\overline{L}}\right](C_{B,1}C_{A,1}{}^n - C_{B,2}C_{A,2}{}^n) \qquad (3.8)$$

For experimental verification of Equation 3.8, it is convenient to express the flux J_B in terms of the experimental quantities from which it is calculated. Experimentally, an aliquot of radiotracer (co-ion B) is added to Side 1 of the membrane-solution system at time zero. At this point there is no tracer on Side 2, but upon initiation of the experiment, some radiotracer co-ion begins to diffuse across the membrane and into the other solution. After a time t, the tracer builds to a concentration $C_{B,2}$ on Side 2 of the membrane. If only a small fraction of the total B diffuses, so that $C_{B,1}$ remains essentially constant, and if the lag time (a few minutes in a typical experiment) represents only a small portion of the total time, t, the flux J_B may be calculated simply.

$$J_B = \frac{-C_{B,2}V_2}{At} \qquad (3.9)$$

In this expression V_2 is the volume of the external solution on Side 2 of the membrane and A is the area of the membrane exposed to the external solution.

Combining Equations 3.8 and 3.9 to eliminate J_B, and rearranging, an expression for the co-ion transported across an ion exchange membrane is obtained which may be experimentally tested and verified.

$$\frac{c_{B,1}}{c_{B,2}} = \frac{V_2 \overline{L}}{At \overline{D}_B k} \left[\frac{1}{c_{A,1}^n} \right] + \left[\frac{c_{A,2}}{c_{A,1}} \right]^n \qquad (3.10)$$

INTERPRETATION OF THE CO-ION TRANSPORT EQUATION

Equation 3.10 states that the ratio of the concentrations of co-ion B on either side of the membrane, at any given time, is inversely proportional to some fractional power, n, of the bulk co-ion A concentration on Side 1 of the membrane. The concentration of species A on Side 2 of the membrane also appears in this expression. However, it will be later shown that the second term of Equation 3.10 is negligible when compared to the first under most conditions. The quantities V_2, $\overline{L}$, and A are parameters relating to the physical design of the system. The inverse dependence upon t is a consequence of the transport being governed by a simple diffusional process. The diffusion coefficient, $\overline{D}_B$, of co-ion B in the membrane may be regarded as constant for any membrane which is predominantly in a particular form. The quantities n and k are em-

pirical and must be determined experimentally from distribution
measurements (see Chapter IV).

The absence of the capacity from Equation 3.10 should not be
taken to mean that the transport rate of co-ion B is independent of
capacity, because k is certainly affected by changes in this quantity,
and $\bar{D}_B$ and n may also be. Thus, as the ion exchange capacity of a
membrane approaches zero, the difference between the internal and ex-
ternal solution decreases, until at zero capacity, equal co-ion levels
would exist in both phases, and k would approach unity.

The following chapters will describe the experimental evaluation
of the co-ion transport theory as here presented, with the co-ion dis-
tribution between the solution and membrane being given in Chapter IV,
and the overall transport data in Chapter V.

CHAPTER IV

EXPERIMENTAL EVALUATION OF THE CO-ION DISTRIBUTION

In this chapter, the co-ion distribution derived in Equation 3.6

$$\frac{\overline{C}_B}{C_B} = kC_A^{\,n} \qquad\qquad (3.6)$$

is verified experimentally.

Expressed logarithmically,

$$\log\left[\frac{\overline{C}_B}{C_B}\right] = n \log C_A + \log k \qquad\qquad (4.1)$$

Thus, a log-log plot of $\overline{C}_B/C_B$ versus C_A should be a straight line of slope n and intercept log k. A least squares analysis permits evaluation of n and k.

EXPERIMENTAL

Reagents

All chemicals used in this work were reagent grade with the ex-

ception of the cesium salts, which were labelled "pure" and were ob-
tained from E. H. Sargent and Company, Chicago, Ill. The radiotracers
used were ^{137}Cs (30 years, 0.662 MEV γ) and ^{22}Na (2.58 years, 1.274 MEV γ).
These isotopes were carrier-free and diluted with water to the appro-
priate activity levels. In the case where a mixed electrolyte-radio-
isotope system was employed, such as ^{137}CsCl tracer in a NaCl solution,
the bulk electrolyte was spiked to 10^{-5} $\underline{M}$ with inactive salt of the
tracer. This was done to diminish the chances of anomalous chemical
behavior of extremely low trace concentrations.

Procedure

A piece of anion exchange membrane weighing about 30 mg was
equilibrated with the desired bulk electrolyte for at least 24 hours.
The equilibrating solution was changed several times to insure com-
pleteness of conversion to the desired form. After the equilibration
step, the membrane was removed from the solution. Excess solution
adhering to the surface was blotted off with tissue, and the membrane
was weighed. The relative standard deviation of blotting and weighing
the membrane for triplicate determinations was about 0.8%.

Next, the membrane was placed in a small test tube containing
2.0 ml of solution identical to that used in the equilibration step.
Then, a 10 μl aliquot of the radiotracer was added to the tube, the
contents were well mixed, stoppered, and allowed to stand for an ad-
ditional 24 hours in order to achieve uniform distribution of the

tracer between the two phases.

At the end of the second 24-hour period, the membrane was removed for counting from the tracer solution and rinsed in two successive portions of water to remove the last traces of adhering bulk solution and the radioactivity therein. When this rinsing was not done, the measured membrane tracer concentration was invariably too high. The total time in the wash solutions was approximately 15 seconds, after which the membrane was placed in a counting tube containing 2.0 ml water.

In the washings, the forceps used in handling the membrane were rinsed well and dried in order to eliminate cross contamination from one solution to the next. Prior to the actual experiments, an evaluation of the rinsing procedure had been carried out and it was found that the above process optimized the two principal and competing sources of error; that of adhering external electrolyte solution containing radiotracer, and that of leaching the tracer from the membrane proper.

An aliquot, usually 100 μl, of the bulk solution containing the radiotracer was removed for counting from the test tube in which the equilibration had taken place and was diluted with 2.0 ml of water.

All samples containing the radioisotope were made up to 2.0 ml with water in a polystyrene counting tube (12 mm in diameter and 75 mm in length) in order to obtain a uniform counting geometry. Membrane samples were allowed to stand for a day before counting in order to

leach the tracer co-ion from the membrane into the aqueous solution.
When the tubes containing membrane were counted without allowing time
for much leaching to occur, the activity data were quite erratic, prob-
ably due to non-uniformity in the counting geometry.

The counting equipment was made by Baird-Atomic, Cambridge, Mass.
It included a well-type scintillation detector (Model 810c), a scaler-
discriminator (University II Series, Model 530), and a printout re-
corder (Model 620). The radioactive samples were usually counted for
five minutes, and if less than 10,000 counts were obtained for a given
sample in this time interval, triplicate five minute counts were then
made, not only to reduce counting error, but also to reveal any chance
or grossly erroneous counts. Membrane samples always had less than
10,000 counts per five minutes.

The radioactivities of the membrane and solution phases were ex-
pressed in terms of counts/ml/min. The activity ratio of these two
phases is identical to the concentration ratio of co-ion B, and gives
the left side of Equation 3.6.

CO-ION DISTRIBUTION DATA

In this work, the co-ion distribution was obtained for two classes
of electrolytes, AX and A_2X. Within each class, three chemical systems
were studied, including: $^{22}NaCl$ - NaCl, $^{137}CsCl$ - NaCl, $^{137}CsCl$ - CsCl,
$^{22}Na_2SO_4$ - Na_2SO_4, $^{137}Cs_2SO_4$ - Na_2SO_4, and $^{137}Cs_2SO_4$ - Cs_2SO_4. Each
system was investigated at five bulk electrolyte concentrations: 0.100,

0.075, 0.050, 0.025, and 0.010 $\underline{M}$, with duplicate determinations made in all cases.

Table 4.1 shows typical data for a co-ion distribution between solution and membrane phases for systems containing chloride or sulfate as counter-ions, Cs as co-ion A, and ^{137}Cs as co-ion B. The data are shown also in Figure 4.1. The lines drawn on these plots are those obtained by a least squares analysis. From the slope of the plot a value of n is found, while k is on the axis of ordinates at $C_A = 1$ (log C_A equal to zero). Appendix III contains the raw data and sample calculations for these systems.

The values of n and k for the six systems studied are shown in Table 4.2. Inspection of the values of n reveals it to be essentially independent of the chemical natures of the trace co-ions for a given counter-ion. However, on changing the counter-ion from a univalent species to a divalent one, the value of the exponent n is decreased by about 4-fold. The quantitative significance of this change is not known, because the effect of counter-ion charge is not included in the distribution equation (Equation 3.6). The quantity k is also essentially independent of the chemical natures of the co-ion species (A and B) for a given counter-ion, but it does increase (approximately doubles) on changing from the chloride system to the sulfate.

The standard deviations of the values of n and k are also shown for each system in Table 4.2. For n, the standard deviations range from 2.4 to 13.2 percent, with a median value of 9.8%. There appears to be

TABLE 4.1

^{137}Cs CO-ION DISTRIBUTION BETWEEN CsCl AND Cs_2SO_4 SOLUTIONS

AND ANION EXCHANGE MEMBRANES

c_A, $\underline{M}$	$\bar{c}_B/c_B$
$^{137}CsCl-CsCl$	
0.100	0.00490
0.100	0.00503
0.075	0.00330
0.075	0.00373
0.050	0.00243
0.050	0.00209
0.025	0.00151
0.025	0.00130
0.010	0.00057
0.010	0.00110
$^{137}Cs_2SO_4-Cs_2SO_4$	
0.200	0.0226
0.200	0.0288
0.150	0.0238
0.150	0.0243
0.100	0.0246
0.100	0.0246
0.050	0.0235
0.050	0.0196
0.020	0.0178
0.020	0.0176

FIGURE 4.1

LOG-LOG PLOT OF $\overline{C}_B/C_B$ VERSUS C_A SHOWING LEAST SQUARES SLOPES

AND INTERCEPTS
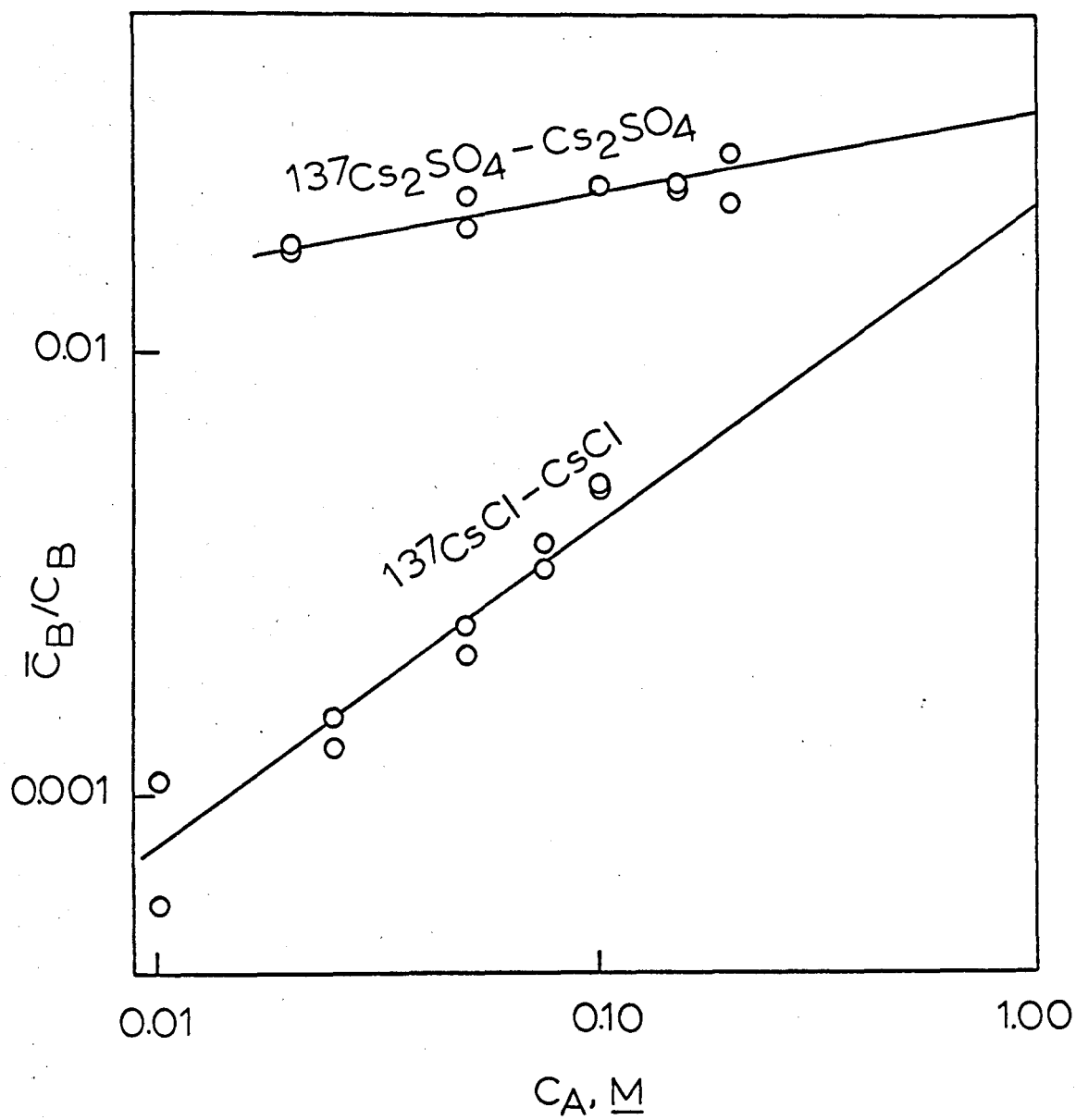
TABLE 4.2

EVALUATION OF n AND k FROM CO-ION DISTRIBUTION MEASUREMENTS

Solution Electrolyte	Tracer Electrolyte	n	k	Relative Standard Deviation, %	
				In n	In k
NaCl	^{22}NaCl	0.82	0.028	2.4	2.3
NaCl*	^{137}CsCl	0.77	0.025	10.8	9.1
CsCl	^{137}CsCl	0.72	0.018	13.2	9.9
Na_2SO_4	$^{22}Na_2SO_4$	0.19	0.038	4.1	1.0
Na_2SO_4**	$^{137}Cs_2SO_4$	0.16	0.035	8.8	1.8
Cs_2SO_4	$^{137}Cs_2SO_4$	0.16	0.037	12.2	1.3

*   Contains 10^{-5} $\underline{M}$ CsCl as carrier
** Contains 10^{-5} $\underline{M}$ Cs_2SO_4 as carrier

no significant difference in the error levels of n in the chloride
and sulfate systems, even though the value of n itself differs greatly.

The values of k are considerably more precise in systems with di-
valent counter-ions than in systems with univalent counter-ions, the
median standard deviations being around 1.3 and 9.1%, respectively.
This would be expected as the slope, n, is quite low for the sulfate
system, so that a given error in slope yields only a small error in
the intercept. For the chloride systems, n is large and as a result,
the error in k is quite sensitive to small errors in slope.

Attempts were made to measure the distribution of a divalent co-
ion between the external solution and membrane phases. The system tested
had $^{133}BaCl_2$ as the tracer electrolyte and $BaCl_2$ as the bulk electrolyte.
However, five days of leaching with water failed to remove the radio-
active ^{133}Ba from the resin phase, indicating that barium has a high
degree of specificity for the membrane. As a result, further investi-
gation of the distribution of divalent co-ions was not attempted.

The lack of dependence of n and k upon the chemical natures of
the co-ion species, both A and B, indicates a low degree of chemical
interaction between the co-ions in the membrane phase. On the other
hand, the definite dependences of n and k upon the charge type of the
counter-ion indicates a high degree of charge interaction between the
co-ions and counter-ions in the membrane phase. Considering the com-
position of the membrane phase, it would not be surprising if co-ions

existed principally in ion pair aggregates with counter-ions. Such ion

pairing has been postulated by other workers (22)(46).

CHAPTER V

VERIFICATION OF THE CO-ION TRANSPORT EQUATION

In Chapter III an equation was developed describing the transport of the tracer co-ion B, from one solution to another through an ion exchange membrane as a function of solution composition, time, and other physical parameters.

$$\frac{C_{B,1}}{C_{B,2}} = \frac{V_2 \overline{L}}{At \overline{D}_B k} \left[\frac{1}{C_{A,1}{}^n} \right] + \left[\frac{C_{A,2}}{C_{A,1}} \right]^n \qquad (3.10)$$

This chapter describes the experimental verification of Equation 3.10. The dependence of $C_{B,1}/C_{B,2}$ upon each variable in the equation is treated separately, except the membrane thickness which cannot be varied.

Equation 3.10 may be rearranged as follows:

$$\frac{C_{B,1}}{C_{B,2}} - \left[\frac{C_{A,2}}{C_{A,1}} \right]^n = \frac{V_2 \overline{L}}{At \overline{D}_B k} \left[\frac{1}{C_{A,1}{}^n} \right] \qquad (5.1)$$

Further simplication may be achieved by setting

$$C_{A,1} = C_{A,2} \qquad (5.2)$$

in all experiments except those in which the parameter $C_{A,2}$ itself is varied. Then, Equation 5.1 becomes

$$\frac{\bar{C}_{B,1}}{C_{B,2}} - 1 = \frac{V_2 \bar{L}}{At \bar{D}_B k} \left[\frac{1}{C_{A,1}^n} \right] \tag{5.3}$$

which is the form used to test the dependence of $C_{B,1}/C_{B,2}$ upon all parameters except $C_{A,2}$.

The dependence of $C_{B,1}/C_{B,2}$ upon $C_{A,1}$ shown in Equation 5.3 was established for several different chemical systems, including the following tracer electrolyte (containing co-ion B) - bulk electrolyte (containing co-ion A) pairs: $^{22}NaCl$ - NaCl, $^{137}CsCl$ - NaCl, $^{137}CsCl$ - CsCl, $^{22}Na_2SO_4$ - Na_2SO_4, $^{137}Cs_2SO_4$ - Na_2SO_4, $^{137}Cs_2SO_4$ - Cs_2SO_4, $^{110m}AgNO_3$ - $AgNO_3$, and $^{133}BaCl_2$ - $BaCl_2$. Among these systems, two were studied intensively for all the variables present in Equation 3.10: $^{137}CsCl$ - NaCl with an univalent counter-ion, and $^{137}Cs_2SO_4$ - Na_2SO_4 with a divalent counter-ion, chosen because co-ions A and B are well defined and chemically different in both cases.

EXPERIMENTAL PROCEDURE

All reagents and radiotracers used in this work were the same as described in Chapter IV, along with two more radioisotopes, $^{133}BaCl_2$ (7.2 years, 0.081 MEV γ) and $^{110m}AgNO_3$ (253 days, 0.44 MEV γ). The

specific activity of the $^{133}BaCl_2$ was approximately 1.5 mc/mg Ba.

The physical design of the cells was the same as that previously used by Blaedel and coworkers (4)(6) (See Appendix I, Figure I, for a schematic of the cells).

The following procedure was used in all co-ion transport determinations. The anion exchange membrane in the cells was converted to the desired form by a 24-hour equilibration with the appropriate bulk electrolyte containing co-ion A at the concentration level to be used later in the actual experiments. Two hours before a determination was initiated, the cells were emptied, rinsed twice with water, and refilled with the same tracer-free electrolyte used earlier. After two hours, the cells were again emptied, and this time rinsed with the same electrolyte solution to be used in the following experiment. Excess solution adhering to the membrane and cell walls was blown out by brief passage of a stream of nitrogen through the cells, care being taken not actually to dry these surfaces.

A 2.0 ml aliquot of the desired bulk electrolyte solution was added to each compartment of the cells. Then, at time zero, a 10 μl portion of radiotracer containing co-ion B was added to Solution 1 with mixing. The cells were stoppered and placed in a circulating water bath thermostated at 25.0 ± 0.2 °C. Four magnetic stirring motors at the bottom of the bath turned a stirring bar within each cell compartment.

At the end of 24 hours, the cells were sampled by means of a micropipet and syringe combination. Usually 100 μl aliquots were taken from each compartment, placed in a counting tube, and diluted with enough water to give a fixed counting volume of 2.0 ml. Generally, a given system was sampled only once, to prevent volume changes that would result from removing experimental samples. After each run, the cells were emptied, rinsed twice with water, and then leached for 24 hours with the electrolyte to be used next.

The samples containing radioisotope were counted using the equipment previously described. After correcting the activity of the samples for background, the ratio of the tracer in Solution 1 to Solution 2, $C_{B,1}/C_{B,2}$, was calculated. This manner of handling the data was the simplest, since the tracer ratio of co-ion B on the two sides of the membrane is identical to its concentration ratio.

EFFECT OF TIME

The dependence of the tracer ratio, $C_{B,1}/C_{B,2}$, upon time was studied with the above experimental procedure, except that a series of aliquots was withdrawn from each compartment of the cells at various times. In the experiments reported here, 100 μl of solution was removed from each compartment at 2, 4, 6, 8, and 24 hours. These samples were then diluted and assayed for the radiotracer activity.

In removing 100 μl (5% of the total volume) from each compartment

at different times, another parameter, V_2, in Equation 3.10 was varied. Since only the effect of time was desired in this study, Equation 3.10 was tested in the following form, which provided corrections for the withdrawal of sample aliquots at various times.

$$\left[\frac{C_{B,1}}{C_{B,2}} - 1\right]\frac{1}{V_2} = \frac{\overline{L}}{At\overline{D}_B k}\left[\frac{1}{C_{A,1}{}^n}\right] \qquad (5.4)$$

Here the quantity $((C_{B,1}/C_{B,2}) - 1)/V_2$ should be inversely proportional to t, and a log-log plot of this quantity versus t should yield a straight line with a slope of -1.

Table 5.1 shows the data obtained for the dependence of the tracer ratio on time for the two systems studied, each at five different concentration levels. In all cases the bulk electrolyte concentration ratio across the membrane was unity. All values of the modified tracer ratio are the means of four individual determinations, with a median relative standard deviation around 10%.

Figure 5.1 shows the data of Table 5.1 on a log-log plot. The experimentally determined slopes of these lines, which are the negative values of the t exponent, were calculated by a least squares analysis and are also reported in Table 5.1. For the $^{137}CsCl$ - NaCl system, the median value of the exponent is -1.04, while for the $^{137}Cs_2SO_4$ - Na_2SO_4 system it is -1.00. All the other systems listed earlier were

TABLE 5.1

DEPENDENCE OF THE CO-ION TRANSPORT ON TIME

$C_{A,1}$, $\underline{M}$	$\left[\dfrac{C_{B,1}}{C_{B,2}} - 1\right]\dfrac{1}{V_2}$					Slope, or Negative Exponent of t
	2 hr.	4 hr.	6 hr.	8 hr.	24 hr.	

^{137}CsCl-NaCl

$C_{A,1}$, $\underline{M}$	2 hr.	4 hr.	6 hr.	8 hr.	24 hr.	Slope
0.100	870	457	280	222	71.9	−1.01
0.075	1480	574	468	270	93.1	−1.10
0.050	2540	695	440	368	114	−1.20
0.025	2360	1580	917	641	194	−1.04
0.010	3530	2740	1490	1190	329	−0.99
					Median	−1.04

^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$

$C_{A,1}$, $\underline{M}$	2 hr.	4 hr.	6 hr.	8 hr.	24 hr.	Slope
0.200	174	78.9	49.6	38.5	13.6	−1.02
0.150	176	97.9	57.8	46.4	15.2	−1.00
0.100	146	82.6	54.3	40.8	13.9	−0.96
0.050	444	136	66.7	41.6	16.2	−1.32
0.020	228	112	73.9	60.0	19.6	−0.98
					Median	−1.00

FIGURE 5.1

DEPENDENCE OF THE CO-ION TRANSPORT ON TIME
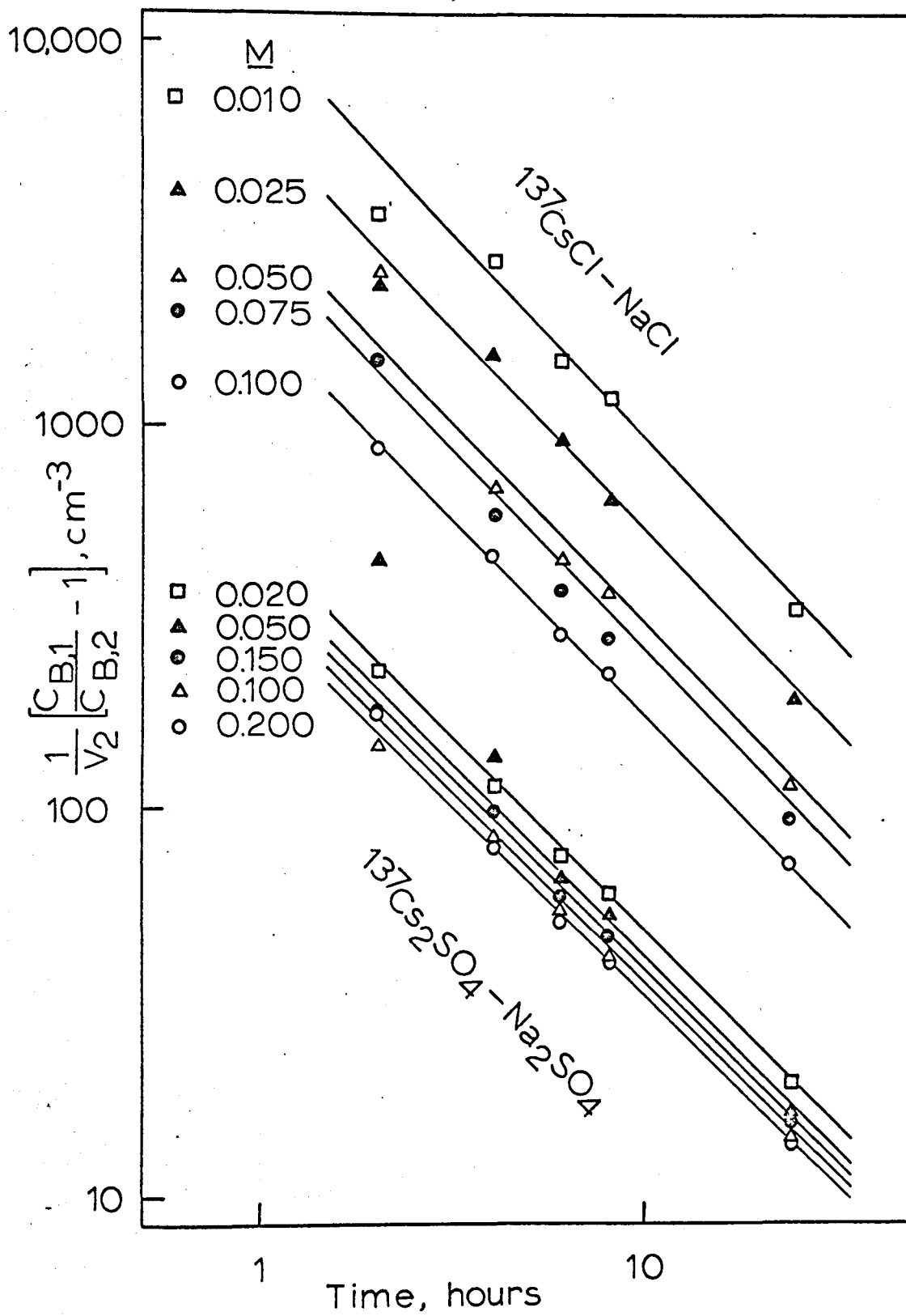
studied in the same way, except for $^{110m}AgNO_3$ - $AgNO_3$ and $^{133}BaCl_2$ - $BaCl_2$. The median values of the t exponent are given in Table 5.2 (detailed data not shown). The average of all medians is -1.00 with a relative standard deviation of 3.4%. This shows conclusively the first order dependence of the tracer ratio on reciprocal time.

Because of the finite thickness of the membrane, there is a short hold-up time after the initiation of the experiment and before steady state transport is reached. Theoretically, the time used in these experiments should be reduced by the duration of this hold-up time, but it is only of the order of a few minutes, which is negligible. It should also be noted that never more than a small amount of co-ion B was ever transported across the membrane. Consequently, the concentration of B on Side 1 of the membrane was considered constant throughout the experiment.

The data presented in Tables 5.1 and 5.2 could also be used to show the dependence of the tracer ratio upon $C_{A,1}$. However, as the cells were sampled several times, a higher error level was introduced. Therefore, additional experiments were carried out (see following section) instead of employing the data obtained in this section.

EFFECT OF $C_{A,1}$

According to Equation 3.10, the amount of co-ion B transported through the ion exchange membrane in a given time interval is de-

TABLE 5.2

SUMMARY OF SLOPES OF LOG TRANSPORT-LOG TIME PLOTS

System	Median Slope, or Negative Exponent of t **
^{22}NaCl-NaCl	-0.98
^{22}NaCl-NaCl*	-1.06
^{137}CsCl-NaCl	-1.04
^{137}CsCl-NaCl*	-1.04
^{137}CsCl-CsCl	-1.00
^{137}CsCl-CsCl*	-1.00
^{22}Na$_2$SO$_4$-Na$_2$SO$_4$	-0.96
^{22}Na$_2$SO$_4$-Na$_2$SO$_4$*	-0.98
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	-1.00
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$*	-0.97
^{137}Cs$_2$SO$_4$-Cs$_2$SO$_4$	-0.97
^{137}Cs$_2$SO$_4$-Cs$_2$SO$_4$*	-0.97
Average	-1.00

*   These values were obtained for $C_{A,1}/C_{A,2}$ = 10, instead of unity, as in the case of all other data.

** Median of five values of the t exponent determined at $C_{A,1}$ = 0.100, 0.075, 0.050, 0.025, and 0.010 $\underline{M}$ for the chloride systems and at $C_{A,1}$ = 0.200, 0.150, 0.100, 0.050, and 0.020 $\underline{M}$ for the sulfate systems.

pendent upon the bulk electrolyte concentration, $C_{A,1}$, on Side 1 of the membrane. The dependence is not first order, however, but rather is fractional, as indicated by the exponent n in Equation 3.10.

Experimental work to determine the effect of $C_{A,1}$ on the tracer ratio was carried out over the range of 0.001 to 2.00 M for the ^{137}CsCl-NaCl and ^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$ systems, the majority of the measurements being restricted to the range of 0.01 to 0.20 M. The ratio of the co-ion A concentrations, $C_{A,1}/C_{A,2}$, was unity at all times.

Table 5.3 gives the data for the transport of co-ion B through the membrane as a function of the concentration of A on Side 1 of the membrane. All points were those taken 24 hours after the initiation of the experiment. Each value is the average of four individual determinations, with a median relative standard deviation of 6.0%. Examples of typical raw data are found in Appendix IV. These same data are shown graphically in Figure 5.2 with log (($C_{B,1}/C_{B,2}$) - 1) being plotted versus log $C_{A,1}$. The straight lines drawn on the graph are those obtained by a least squares analysis of all points between 0.01 and 0.20 M, inclusive. The concentration ranges above 0.20 M illustrate deviations from linearity and departures from Equation 3.10, perhaps due to ion pairing in the more concentrated external solutions.

For the ^{137}CsCl-NaCl system, the value of the slope, -n, from the log-log plot is 0.76, with a relative standard deviation of 3.9%. The n for the sulfate system is 0.16. The relative standard deviation is

TABLE 5.3

DEPENDENCE OF THE CO-ION TRANSPORT ON $C_{A,1}$

$C_{A,1}$, $\underline{M}$	$(C_{B,1}/C_{B,2}) - 1$
^{137}CsCl-NaCl	
1.000	40.8
0.500	50.0
0.250	72.4
0.100	128
0.075	144
0.050	216
0.025	353
0.010	717
0.001	5030
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	
2.000	30.4
1.000	24.7
0.500	22.4
0.200	21.7
0.150	22.6
0.100	24.3
0.050	26.0
0.020	32.2
0.002	68.8

FIGURE 5.2

DEPENDENCE OF THE CO-ION TRANSPORT ON $C_{A,1}$

The y-axis is labeled $\dfrac{C_{B,1}}{C_{B,2}} - 1$ ranging from 10 to 10,000. The x-axis is labeled $C_{A,1}$, $\underline{M}$ ranging from 0.001 to over 1.00. The upper curve is labeled $^{137}CsCl - NaCl$ and the lower curve is labeled $^{137}Cs_2SO_4 - Na_2SO_4$.
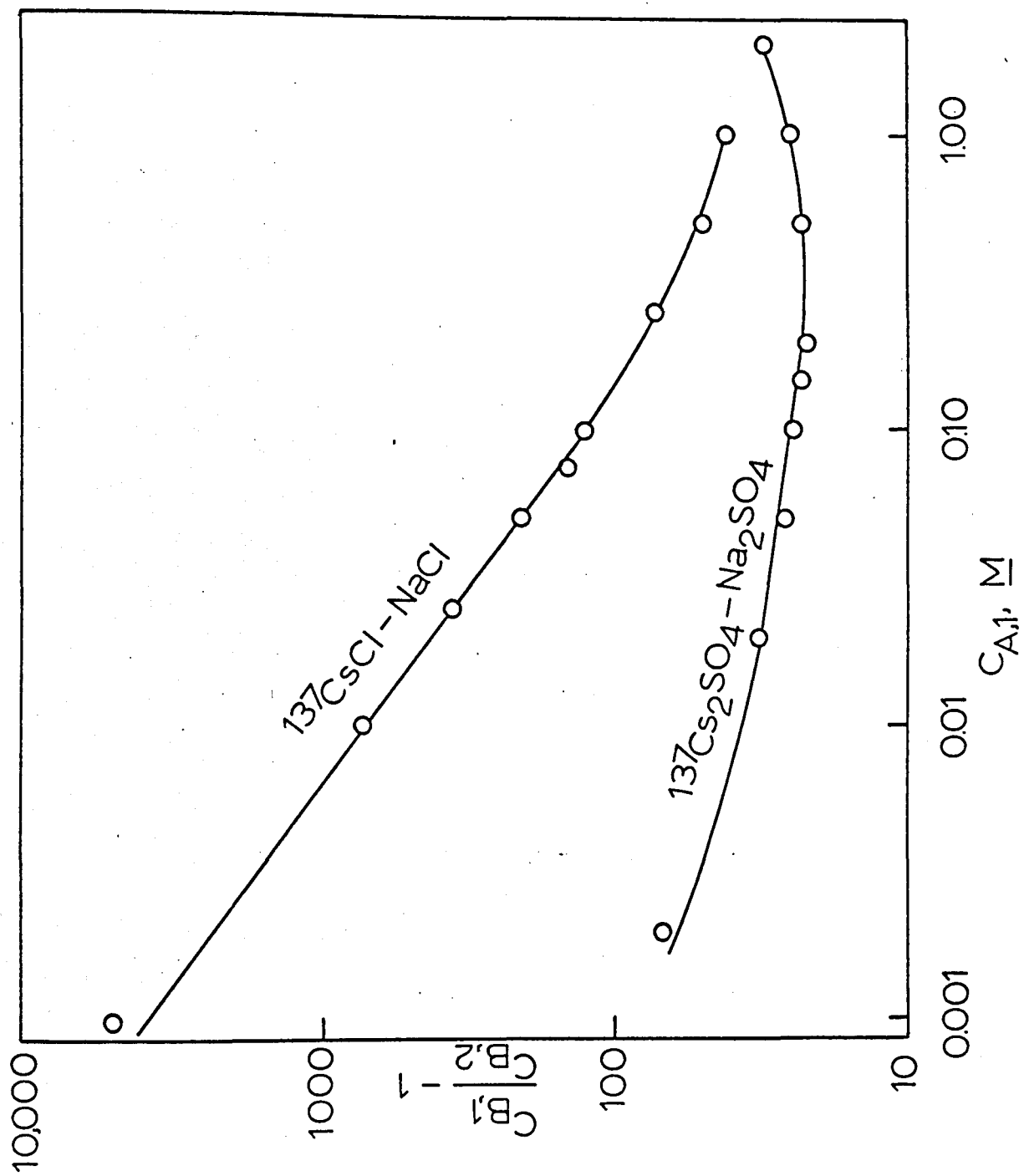
10.6%. The intercepts at $C_{A,1}$ = 1.0 $\underline{M}$ are 21.6 and 15.6, respectively.

EFFECT OF $\underline{C}_{A,2}$

Equation 3.10 states that the tracer ratio, $C_{B,1}/C_{B,2}$, is dependent upon $C_{A,2}$. However, experimental work has shown that the effect of $C_{A,2}$ upon the transport is negligible.

To verify the dependence, or lack of it, of the tracer ratio on $C_{A,2}$, a series of experiments for both the $^{137}CsCl$-$NaCl$ and $^{137}Cs_2SO_4$ - Na_2SO_4 systems was carried out in which $C_{A,1}$ was held constant at 0.01 $\underline{M}$ for the chloride system and 0.02 $\underline{M}$ for the sulfate, while $C_{A,2}$ was either 0.10, 0.01 or 0.001 $\underline{M}$ for chloride or 0.20, 0.02 or 0.002 $\underline{M}$ for sulfate. The amount of co-ion B transported across the membrane in 24 hours was then measured, with data shown in Table 5.4. All values are the means of four individual determinations with a median relative standard deviation of 7.8%. It may be seen that the tracer ratio, $C_{B,1}/C_{B,2}$, shows practically no variation when $C_{A,1}$ is fixed, even though $C_{A,2}$ is varied over a 100-fold range.

The preceding experiments were repeated, but with $C_{A,1}$ fixed at higher concentrations: 0.10 $\underline{M}$ or 0.20 $\underline{M}$ for the chloride or sulfate systems, respectively. Results are shown in Table 5.4, and the conclusion is the same: when $C_{A,1}$ is fixed, $C_{B,1}/C_{B,2}$ shows practically no variation even though $C_{A,2}$ is varied from 0 to 0.20 $\underline{M}$. Interpreted in relation to Equation 3.10, this means that the term involving $C_{A,2}$

TABLE 5.4

DEPENDENCE OF THE CO-ION TRANSPORT ON $C_{A,2}$

$C_{A,1}$, $\underline{M}$	$C_{A,2}$, $\underline{M}$	$C_{A,2}/C_{A,1}$	$C_{B,1}/C_{B,2}$
^{137}CsCl-NaCl			
0.010	0.100	10.00	735
0.010	0.010	1.00	718
0.010	0.001	0.10	752
0.100	0.100	1.00	129
0.100	0.010	0.10	133
0.100	0	0	124
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$			
0.020	0.200	10.00	30.6
0.020	0.020	1.00	33.2
0.020	0.002	0.10	33.9
0.200	0.200	1.00	22.7
0.200	0.020	0.10	21.6
0.200	0	0	22.6

is essentially negligible over the range of conditions studied.

EFFECT OF V_2

The volume of Solution 2, V_2, appears in the numerator of Equation 3.10. Therefore, the co-ion tracer ratio, $C_{B,1}/C_{B,2}$, should be directly proportional to this quantity. To test this dependence, the same basic experiments were run as earlier described, except that the volume of Solution 2 was varied from 1.0 to 3.0 ml.

Table 5.5 shows the variation of the tracer ratio with changes in V_2 for both the chloride and sulfate systems. In these experiments, the co-ion A concentration was the same in both solutions, and the ratio $C_{A,2}/C_{A,1}$ was always unity. All samples were taken from the cells 24 hours after the start of the experiments, with each value being the average of four determinations. The median relative standard deviation is 7.8%. A log-log plot (not shown) of the data of Table 5.5 demonstrates the first order dependence of the tracer ratio upon V_2. This dependence is also shown in Table 5.5 by the relative constancy of the ratio $((C_{B,1}/C_{B,2}) - 1)/V_2$ for each of the two systems, in accord with Equation 3.10.

EFFECT OF V_1

Even though the parameter V_2 appears in the co-ion transport expression (Equation 3.10), V_1 does not. It was therefore considered desirable to check whether there was in fact any dependence upon the

TABLE 5.5

DEPENDENCE OF THE CO-ION TRANSPORT ON V_2

$C_{A,1}$, $\underline{M}$	V_2, ml	$(C_{B,1}/C_{B,2}) - 1$	$((C_{B,1}/C_{B,2}) - 1)/V_2$, ml^{-1}
		^{137}CsCl-NaCl	
0.100	1.0	68.1	68
0.100	2.0	128	64
0.100	3.0	176	59
		^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	
0.200	1.0	12.9	13
0.200	2.0	21.7	11
0.200	3.0	30.4	10

volume of Solution 1. Experimentally, the standard procedure was used, holding V_2 constant at 2.0 ml, and varying V_1 from 1.0 to 3.0 ml. The concentration ratio of co-ion A was again set at unity, and all samples were removed from the cells 24 hours after the experiment was initiated.

The lack of dependence of the co-ion B tracer ratio upon V_1 is shown in Table 5.6. Each value is the mean of four individual determinations, with a median relative standard deviation of 8.8%.

EFFECT OF AREA

The co-ion transport is dependent upon the area of the ion exchange membrane exposed to the external solution. The diameter of the normal cell cavity was 1.90 cm, with a resulting membrane area of 2.85 cm^2. To vary this area, new cells had to be constructed for each desired size. Consequently, measurements of the co-ion transport dependence upon area were made on only one additional set of cells, these having an area of 1.27 cm^2.

Experimentally, the same procedures were followed as earlier described. The bulk electrolyte concentration ratios were unity. The data are shown in Table 5.7. All tracer ratios are the means of four individual determinations made at the end of the 24-hour experiments, the median relative standard deviation being 7.8%. Inspection of the last column in Table 5.7 shows fair constancy of the product $A((C_{B,1}/C_{B,2}) - 1)$, in

TABLE 5.6

DEPENDENCE OF THE CO-ION TRANSPORT ON V_1

$C_{A,1}$, $\underline{M}$	V_1, ml	$(C_{B,1}/C_{B,2}) - 1$
	^{137}CsCl-NaCl	
0.100	1.0	134
0.100	2.0	128
0.100	3.0	114
	^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	
0.200	1.0	22.1
0.200	2.0	21.7
0.200	3.0	21.3

TABLE 5.7

DEPENDENCE OF THE CO-ION TRANSPORT ON AREA

$C_{A,1}$	A, cm^2	$(C_{B,1}/C_{B,2}) - 1$	$A((C_{B,1}/C_{B,2}) - 1)$, cm^2
		^{137}CsCl-NaCl	
0.100	1.27	320	406
0.100	2.85	128	365
		^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	
0.200	1.27	51.8	65.8
0.200	2.85	21.7	61.8

accord with Equation 3.10.

EFFECT OF TEMPERATURE

Temperature, while not appearing explicitly in Equation 3.10, does affect the transport of co-ion B across the membrane. If the transport through the membrane resembles an aqueous solution diffusion process, then $\overline{D}_B$ should change by about 2% per degree change in temperature. On the other hand, a temperature coefficient for $\overline{D}_B$ which is much greater than 2% per degree might indicate that the transport through the membrane is associated with a chemical process. To settle this question, co-ion transport studies by the basic experimental procedure were made at 0, 25 and 40 °C. In all cases, the bulk electrolyte concentration ratio was unity. Table 5.8 shows the behavior of the co-ion B tracer ratio with changes in temperature. Each value is the mean of four determinations, with samples taken 24 hours after the initiation of the experiment. The median relative standard deviation is 9.0%.

On inspection of the data, it is clear that the change in the tracer ratio with temperature is around 2-3% per degree for each system studied. Since no other parameter in the experimental procedure and/or equation was altered, the variation of $\overline{D}_B$ alone must have been responsible for these changes in $C_{B,1}/C_{B,2}$. The transport of tracer B co-ion through the membrane phase therefore shows the same temperature dependence as simple diffusional processes in aqueous solutions.

TABLE 5.8

DEPENDENCE OF THE CO-ION TRANSPORT ON TEMPERATURE

$C_{A,1}$, $\underline{M}$	T, $^\circ C$	$(C_{B,1}/C_{B,2}) - 1$	Temperature Coefficient**
		$^{137}CsCl-NaCl$	
0.100	0	248*	
			2.55
0.100	25	128.	
			2.96
0.100	40	81.4	
		$^{137}Cs_2SO_4-Na_2SO_4$	
0.200	0	48.5	
			4.00
0.200	25	21.7	
			2.56
0.200	40	14.7	

* Mean of three determinations

** Defined as $\dfrac{\Delta((C_{B,1}/C_{B,2}) - 1)}{\Delta T}$ x $\dfrac{100}{(C_{B,1}/C_{B,2}) - 1}$, percent

DEPENDENCE OF THE CO-ION TRANSPORT ON $C_{A,1}$ FOR ALL SYSTEMS - EVALUATION OF n

The work presented thus far has been concerned with two chemical systems - $^{137}CsCl$ - $NaCl$ and $^{137}Cs_2SO_4$ - Na_2SO_4. These have been studied intensively for all parameters appearing in Equation 3.10, except $\bar{L}$. While no such complete investigation was intended for many other types of substances, it was considered important to find the dependence of the co-ion B tracer ratio upon the concentration of co-ion A in Solution 1 for six additional systems, including $^{22}NaCl$ - $NaCl$, $^{137}CsCl$ - $CsCl$, $^{22}Na_2SO_4$ - Na_2SO_4, $^{137}Cs_2SO_4$ - Cs_2SO_4, $^{110m}AgNO_3$ - $AgNO_3$, and $^{133}BaCl_2$ - $BaCl_2$.

In all these studies, except that of $^{133}BaCl_2$ - $BaCl_2$, five concentration levels for co-ion A in Solution 1 were investigated: 0.100, 0.075, 0.050, 0.025 and 0.010 $\underline{M}$ for univalent counter-ions, and 0.200, 0.150, 0.100, 0.050 and 0.020 $\underline{M}$ for divalent counter-ions. Because of the times required for accurate measurements in the $^{133}BaCl_2$ - $BaCl_2$ system, and because of their low accuracy, only two concentrations were investigated: 0.100 and 0.010 $\underline{M}$. The bulk co-ion A concentration ratio was either 1.0 or 10.0. All systems were sampled periodically (except the $^{133}BaCl_2$ - $BaCl_2$ system which was assayed only at 24 hours). Consequently, V_2 did not remain constant over the entire length of the experiment. Changes in V_2 were taken into consideration by using an average volume of Solution 2 over the time of the experiment. With 100 μl samples taken at

2, 4, 6, 8, and 24 hours, this mean V_2 was found to be 1.68 ml instead of the initial value of 2.0 ml.

A least squares analysis of the data as described previously yielded values of n for each system, the results of which are shown in Table 5.9. All experiments were carried out in quadruplicate. Also shown in Table 5.9 are the relative standard deviations of n for each system studied. These range from 3.2 to 12.9% with a median of 7.5%.

On comparing the systems containing chloride and sulfate, two distinct values of n are obtained; approximately 0.77 for the univalent counter-ion systems and 0.16 for the divalent counter-ion systems. All values of n within a given counter-ion class are essentially the same, being independent of the nature of the co-ion (both A and B). The data for the $^{110m}AgNO_3$ - $AgNO_3$ system are also shown in the table, the value of n being approximately that found for other univalent counter-ion systems. However, due to interaction of the silver ion with the membrane itself (Table 2.2), little reliance can be placed on the data. The $^{133}BaCl_2$ - $BaCl_2$ system was only investigated at two concentration levels, and the high resistance of the membrane to passage of the divalent co-ion makes the value of n highly unprecise. Even so, the data did yield a value of n that was definitely greater than 2.

TABLE 5.9

EVALUATION OF n FOR ALL CHEMICAL SYSTEMS

System	$C_{A,2}/C_{A,1}$	n	Relative Standard Deviation, %
^{22}NaCl–NaCl	1.0	0.75	6.0
^{22}NaCl–NaCl	0.1	0.71	7.1
^{137}CsCl–NaCl	1.0	0.76	3.9
^{137}CsCl–NaCl	0.1	0.78	3.6
^{137}CsCl–CsCl	1.0	0.79	4.0
^{137}CsCl–CsCl	0.1	0.81	5.8
Average		0.77	5.1
^{22}Na$_2$SO$_4$–Na$_2$SO$_4$	1.0	0.19	12.9
^{22}Na$_2$SO$_4$–Na$_2$SO$_4$	0.1	0.15	12.2
^{137}Cs$_2$SO$_4$–Na$_2$SO$_4$	1.0	0.16	10.6
^{137}Cs$_2$SO$_4$–Na$_2$SO$_4$	0.1	0.19	7.9
^{137}Cs$_2$SO$_4$–Cs$_2$SO$_4$	1.0	0.13	7.5
^{137}Cs$_2$SO$_4$–Cs$_2$SO$_4$	0.1	0.16	11.6
Average		0.16	10.4
^{110m}AgNO$_3$–AgNO$_3$	1.0	0.68	3.2
^{133}BaCl$_2$–BaCl$_2$	1.0	> 2	–

CHAPTER VI

THE CO-ION TRANSPORT EQUATION

Summary

Equation 3.10, derived from a combination of the distribution expression relating the co-ion concentrations in the membrane and solution phases and Fick's First Law of Diffusion, was developed in Chapter III. Subsequent chapters gave experimental data in support of this theory.

The co-ion transport equation predicted that the concentration ratio of a trace co-ion B across an ion exchange membrane was a function of time and various physical parameters, as well as the external solution composition. The data presented in Chapter V conclusively show that the first order dependence of the tracer ratio, $C_{B,1}/C_{B,2}$, on the volume of Solution 2, membrane area, time of diffusion, and the membrane diffusion coefficient of co-ion B was as predicted by Equation 3.10. Linearity of the co-ion transport with these parameters was in accord with previous work, summarized by Helfferich (28).

However, the dependence of the transport of tracer co-ion on the solution composition, particularly $C_{A,1}$, was different from that previously stated in the literature. The present study has shown that the distribution of a co-ion between two phases and the dependence of the overall transport of co-ion from one solution to another through

an ion exchange membrane, was dependent upon the external solution concentration of the bulk co-ion A, but to a fractional power, the value of which was dependent upon the charge type of the counter-ion. For chloride systems, the value of the power, n, was about 0.77, while sulfate counter-ions yielded an n of 0.16.

Equations 3.6 and 3.10 contain no arbitrary parameters, even though n and k are empirical. In Chapter IV experimental evaluation of the postulated co-ion distribution expression was shown, and from the data, values of n and k were determined. Then, in Chapter V, work was presented to support the co-ion transport equation, and another value of n was obtained, though not for k. Comparison of the two n's for a given chemical system shows that they are indeed the same (Table 6.1). Therefore, though the quantity n is empirical and chosen to fit the data, it must be emphasized that its choice is not completely arbitrary, since the same value fits two independent and experimentally different sets of data. Comparison of n values is summarized in Table 6.1, which shows the lack of dependence of n upon the chemical identity of co-ions A and B, but which shows the great dependence upon counter-ion charge type. For the chloride counter-ion systems, the mean value of n from all determinations, both distribution and transport studies, was 0.77, with a relative standard deviation of 4.8%. The average n found in the sulfate counter-ion systems was 0.17, the relative standard deviation being 12.4%.

TABLE 6.1

COMPARISON OF VALUES OF n DETERMINED FROM DISTRIBUTION AND TRANSPORT STUDIES

System	$C_{A,2}/C_{A,1}$	Transport n	Distribution n	% Difference*
$^{22}NaCl-NaCl$	1.0	0.75	0.82	−9.3
$^{22}NaCl-NaCl$	0.1	0.71	0.82	−15.3
$^{137}CsCl-NaCl$	1.0	0.76	0.77	−1.3
$^{137}CsCl-NaCl$	0.1	0.78	0.77	+1.3
$^{137}CsCl-CsCl$	1.0	0.79	0.72	+8.9
$^{137}CsCl-CsCl$	0.1	0.81	0.72	+11.1
Average		0.77	0.77	0.0
$^{22}Na_2SO_4-Na_2SO_4$	1.0	0.19	0.19	0.0
$^{22}Na_2SO_4-Na_2SO_4$	0.1	0.15	0.19	−26.7
$^{137}Cs_2SO_4-Na_2SO_4$	1.0	0.16	0.16	0.0
$^{137}Cs_2SO_4-Na_2SO_4$	0.1	0.19	0.16	+15.8
$^{137}Cs_2SO_4-Cs_2SO_4$	1.0	0.13	0.16	−23.1
$^{137}Cs_2SO_4-Cs_2SO_4$	0.1	0.16	0.16	0.0
Average		0.16	0.17	−6.2

* Defined as (Transport n − Distribution n) x 100/Transport n.

DISCUSSION AND COMPARISON WITH OTHER WORK

Through the early 1960's, most workers used the Donnan Law as the basis of co-ion distribution between the resin and solution phases. Though some of this work was not accurate, the Donnan expression was still consistently employed. For a uni-univalent electrolyte, the tracer ratio of co-ion B was predicted to be first order dependent upon the concentration of the bulk co-ion A. In the present study, a fractional power dependence was observed.

The experimental difference from the established ideal Donnan Law is significant. Such deviations were first recognized by Glueckauf and coworkers (10)(18)(19). Using a co-ion distribution expression similar to Equation 3.6 (see Equation 1.9), but based on the counter-ion concentration of the bulk electrolyte instead of the co-ion, they found that the co-ion uptake by the ion exchange membrane was not first order with respect to the external solution concentration, but rather had a fractional dependence. Their value of the exponent for chloride counter-ion systems was approximately 0.25 for all co-ions, whether univalent or trivalent. These observations are at variance with the charge dependent values of 0.77 and 0.17 found in the present work for univalent and divalent counter-ions, respectively. To date, the differences have not been reconciled.

As to the significance of the fractional exponent, only speculative answers can be given. Glueckauf (19) stated that "It must thus be con-

cluded that the fractional power law of the counter-ion concentration is a phenomenon which is inherent in the nature of the organic ion exchangers which have been tested." He then went on to say that since the Donnan Law must apply to a pair of homogeneous phases, the membrane phase therefore was heterogeneous.

From the work in the present study, it is believed that the difference between the observed co-ion behavior and the idealized Donnan Law Behavior is due to the inherent nature of the membrane. However, rather than to invoke the concept of resin heterogeneity to explain these deviations, a mechanism different from the Donnan Law to describe the partitioning of co-ion between the two phases has been developed (Equation 3.6), based on a Freundlich Adsorption Isotherm. The quantity n in this expression is empirical. Thus, any value may be selected for it, and no theoretical significance is attached to its magnitude. The transport equation, Equation 3.10, was developed from the Freundlich expression, and experimental work on the transport of co-ion from Solution 1 to Solution 2 through the ion exchange membrane has been carried out over a concentration range of 0.001 $\underline{M}$ to 2.00 $\underline{M}$. The equation holds for the range of 0.001 to 0.20 $\underline{M}$. Above approximately 0.20 $\underline{M}$, deviations from the predicted behavior occur which are of a sign opposite to those predicted by the Donnan affect, and which cannot be explained by the Donnan mechanism. Complications due to activity effects and ion pairing in the external solutions make evaluation of

the mechanism in this upper concentration region difficult, and the transport mechanism is presently unknown in the high concentration region. At concentrations below 0.001 $\underline{M}$, co-ion transport is very slow, and no work was carried out due to the experimental problems involved. Therefore, no judgment can be made as to whether or not the theory presented in this thesis can be applied to the lower concentration regions.

MEMBRANE PHASE CO-ION DIFFUSION COEFFICIENTS

An important application of the co-ion transport expression is the calculation of the membrane diffusion coefficients. If Equation 3.10 is expressed logarithmically

$$\log \left[\frac{C_{B,1}}{C_{B,2}} - \left(\frac{C_{A,2}}{C_{A,1}} \right)^n \right] = \log \left[\frac{V_2 \overline{L}}{A t \overline{D}_B k} \right] - n \log C_{A,1} \quad (6.1)$$

a log-log plot of the left side of Equation 6.1 versus $C_{A,1}$ would yield a straight line of slope -n and an intercept of log $(V_2\overline{L}/A t \overline{D}_B k)$. Since all parameters except $\overline{D}_B$ are known or measurable, measurement of the intercept permits calculation of $\overline{D}_B$.

A least squares analysis of the data for each system studied gave values for the intercept and its standard deviation. Table 6.2 shows

TABLE 6.2

EVALUATION OF $\overline{D}_B$

System	$C_{A,2}/C_{A,1}$	Ordinate Intercept	Relative Standard Deviation, %	$\overline{D}_B \times 10^7$ cm^2/sec
^{22}NaCl-NaCl	1.0	26.8	4.5	1.95
^{22}NaCl-NaCl	0.1	31.0	4.0	1.69
^{137}CsCl-NaCl	1.0	21.6	5.3	2.42
^{137}CsCl-NaCl	0.1	21.2	5.3	2.47
^{137}CsCl-CsCl	1.0	22.6	5.0	2.31
^{137}CsCl-CsCl	0.1	18.7	6.5	2.80
Average			5.1	2.27
^{22}Na$_2$SO$_4$-Na$_2$SO$_4$	1.0	12.9	8.6	2.62
^{22}Na$_2$SO$_4$-Na$_2$SO$_4$	0.1	15.3	7.1	2.21
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	1.0	15.6	6.9	2.17
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	0.1	13.7	7.7	2.47
^{137}Cs$_2$SO$_4$-Cs$_2$SO$_4$	1.0	14.6	7.1	2.32
^{137}Cs$_2$SO$_4$-Cs$_2$SO$_4$	0.1	12.3	8.8	2.75
Average			7.7	2.42

this data and the values of $\bar{D}_B$ calculated, while Table 6.3 gives the values and relative standard deviations of each parameter contained in the intercept. The mean value of $\bar{D}_B$ for the chloride counter-ion systems is 2.27 x 10^{-7} cm^2/sec, with a relative standard deviation of 17.4%. For the sulfate counter-ion systems, $\bar{D}_B$ is 2.42 x 10^{-7} cm^2/sec and the relative standard deviation is 3.0%. From the data in Table 6.3, a theoretical value of the standard deviation of $\bar{D}_B$ can be calculated roughly from the square root of the sum of the squares of the individual standard deviations. These are 20.6 and 5.9% for chloride and sulfate counter-ion systems, respectively.

At the 20% error level that is involved in the measurements, it therefore appears that there are no significant differences among the membrane diffusion coefficients of co-ions (both Na and Cs) in the different systems that were studied. Specifically, the values of $\bar{D}_B$ for Cs and Na in six chloride counter-ion systems range around 2.3 x 10^{-7} cm^2/sec, though perhaps the membrane diffusion coefficient for sodium co-ion in a NaCl matrix may be slightly smaller than the others reported in Table 6.2. For sulfate counter-ion systems, none of the six values of $\bar{D}_B$ are significantly different from the mean value of 2.4 x 10^{-7} cm^2/sec. In short, at the 20% error level, the membrane diffusion coefficient of the trace co-ion is roughly: (1) the same for ^{22}Na and ^{137}Cs trace co-ions, (2) the same for Na and Cs bulk co-ions, (3) independent of whether the membrane is in the chloride or sulfate form, that is, independent of

TABLE 6.3

INTERCEPT PARAMETERS

Parameter	Value	Relative Standard Deviation, %	Reference (page no.)
$\bar{L}$	0.0153 cm	2.6	21
V_2	2.00 ml	2.5*	67
A	2.85 cm^2	1.0*	69
t	86,400 sec	0.5*	54
k**	0.024	20.2	48
k***	0.037	4.6	48

* The error limits in these quantities were estimated as follows:
$V_2 = 2.00 \pm 0.05$ ml, $A = 2.85 \pm 0.03$ cm^2, and $t = 86,400 \pm 300$ sec.

** Chloride counter-ion systems

*** Sulfate counter-ion systems

the nature of the counter-ion, and (4) independent of the concentration of the bulk co-ion in the external solution.

The independence of $\overline{D}_B$ from the external solution co-ion concentration is expected, as this variable does not significantly affect the conditions within the membrane. As the external co-ion concentration increases, so does the resin phase concentration, but co-ions contribute only a small fraction to the total ionic concentration within the membrane over the concentration ranges studied.

As was concluded from the distribution studies, the absence of any effect of the trace co-ion B identity on the bulk co-ion A and counter-ion identities in the membrane indicates a low degree of chemical interaction between co-ions and counter-ions in this phase. Therefore, it is not surprising that the values of the co-ion B membrane diffusion coefficients are quite similar.

Even the charge of the counter-ion has little effect on the co-ion diffusion coefficient. Charge does affect the distribution of co-ions between the two phases, but apparently, once in the membrane it has little effect. This might well be expected, since when sulfate is the counter-ion, though divalently charged, only half as many ions are in the membrane as compared to the chloride systems. Thus, the counter-ion overall charge density remains essentially the same. By considering Gregor's (21) definition of the membrane phase, it may be considered as a constrained, highly concentrated solution of polyelectrolyte. If this phase is truly

concentrated, then whether two exchange groups are occupied by two chloride ions or one sulfate ion may be inconsequential as far as the mechanism of co-ion diffusion is concerned.

A comparison of diffusion coefficients in the membrane phase and in aqueous solutions for ion B as a co-ion and as a counter-ion is given in Table 6.4. The values of the co-ion $\overline{D}_B$ for sodium and cesium ions are the averages of all $\overline{D}_B$'s in Table 6.2. For B as a counter-ion, values from Blaedel and Haupert (7) are presented. These were measured using the AMF C-103-DD cation exchange membrane (identical to the AMF A-104-EB membrane except that the exchange groups are of the sulfonic acid type rather than the quaternary ammonium variety). While the comparison of membrane diffusion coefficients for a given ion in two different types of membranes is admittedly cloudy, it is believed that the order of magnitude of these values may be compared.

As is noted from Table 6.4, the membrane diffusion coefficient of co-ion B is about two orders of magnitude smaller than those found in aqueous solutions. Also, the membrane diffusion coefficients of B as counter-ions are much smaller than their solution counterparts, and are of the same order of magnitude as those found for the co-ion in the resin phase. This was expected from previous work where the value of the membrane diffusion coefficients for the counter-ion was usually 2-3 times that of the co-ion ((28) p. 353).

TABLE 6.4

COMPARISON OF MEMBRANE AND SOLUTION PHASE DIFFUSION COEFFICIENTS

Ion	$D \times 10^7$, cm^2/sec		
	In membrane, as co-ion	In membrane, as counter-ion*	In aqueous solution**
Na^+	2.12	9.04	133
Cs^+	2.46	5.11	205

* Counter-ion membrane diffusion coefficients in the AMF C-103-DD membrane (7).

** Calculated from limiting equivalent conductivities (45).

Among the more important reasons postulated for the decrease in the co-ion diffusion coefficient in the membrane as compared to its value in aqueous solutions, two appear most likely (43): the increased tortuosity which the co-ion faces within the resin matrix as it must find its way through the organic network, and electrostatic repulsion of the co-ion by fixed ion exchange groups. Both arguments are plausible, though the former seems more reasonable to account for the magnitude of the effect. The ion exchange membranes used in this work actually consist of quaternary ammonium groups attached to polystyrene units, which in turn are supported by a polyethylene grid having no ion exchange capacity. This supporting material is essentially opaque to the ionic species, which means that the diffusion coefficients measured in such membranes are probably smaller than those that would characterize a membrane composed of pure ion exchange material.

ERROR DISCUSSION

The work presented in Chapters IV, V and VI summarizes the experimental verification of the co-ion transport through ion exchange membranes as predicted by Equation 3.10. The experimental error is high, the relative standard deviation being of the order of 10% for quadruplicate samples. However, this error level cannot be significantly reduced without greatly complicating the work.

The errors arise from three main sources: the sampling of the

radioactive species, the measurements of the radioactivity, and the variation in the thickness of the membrane. The last factor was discussed in Chapter II and will not be further considered. Other errors such as solution preparation, pipetting, and dilutions are negligible compared to the above three factors.

Sampling of the radioactive species must be subdivided into two sections: distribution and transport studies. In the distribution experiments, the relative errors in the determination of n and k are quite high, but explainably so. When measuring radiotracer co-ion activity ratios (membrane to solution) of 1:100 at best and less than 1:1000 in some cases, the slightest contamination of the membrane sample with the equilibrating solution can cause significant error, and such contamination has probably caused large errors in the work of some early investigators. However, the membrane samples cannot be rinsed too long, otherwise leaching of the desired radiotracer co-ion from within the membrane will occur. Thus, errors of contamination versus those of over-rinsing must be optimized.

In the transport studies, withdrawal of the radioactive samples from the cells would appear to be relatively easy and error-free. However, this was not the case. The usual sample aliquot taken from each compartment was 100 μl, using a micropipet-syringe combination. Even though this volume is small, it is still a significant fraction of the total volume, and errors of 1-2% are not unlikely. The micro-

pipet, being calibrated to contain, then had to be rinsed into the counting tube. This was accomplished by injecting the radiotracer aliquot into 1.9 ml water and then rinsing the pipet twice with the tracer-water mixture. Between samples, the pipet was washed well with soapy water, distilled water, and reagent grade methanol to eliminate cross contamination.

The other major source of error in the experiment was the counting of the radioactivity itself. Background corrections had to be made to all measured tracer activities and the size of the correction often was a significant fraction of the sample activity. However, the bulk of the error associated with the gamma scintillation counting arose from the very nature of the experiments. Since co-ions are virtually excluded from the ion exchange membrane, the rate of transport of tracer co-ion B across this barrier is low, resulting in low activities in Solution 2.

Radioactive decay is a random process. The error associated with any determination of tracer activity is $N^{\frac{1}{2}}$, where N is the number of counts recorded. For many of the Solution 2 transport studies and membrane distribution studies samples, the radioactivity count in five minutes was 500 or less. Here $N^{\frac{1}{2}}$ is 22, or a 4.5% probable error. To reduce these errors, and to diminish the possibility of chance gross errors, all samples that had activities less than 10,000 counts per 5 minutes were counted three times and averaged.

Variation of the membrane thickness cannot be completely elimi-nated unless better quality membranes become available from the manu-facturer. However, both the above errors might be reduced by the following operations. A larger cell would allow the sampling of larger aliquots from each compartment, reducing the sampling error and at the same time increasing the total activity measured. Even so, increasing the cell size would not be without disadvantages. More radiotracer would be needed in order to maintain the same specific activity in Solution 1, and also, problems of locking the membrane between the two Leucite blocks might well arise. However, some modi-fications of the cell design and/or experimental procedure could prob-ably be profitably undertaken.

IMPROVEMENTS OF THE CO-ION TRANSPORT EQUATION

Several improvements to the co-ion transport equation are still needed, both theoretically and experimentally. However, before some of the experimental factors can be improved, better membranes are needed. Though ion exchange membrane technology has come a long way since Juda (33) first patented synthetic membranes in 1953, problems like the variation in membrane thickness still exist, as stated in Chapter II.

Experimental evaluation of the co-ion distribution between ex-ternal solution and membrane phases is unprecise, with duplicated de-terminations often varying by 20% or more. Improved techniques for

washing the electrolyte-tracer solution from the membrane surface must be developed to improve the measurements.

Theoretically there are certain factors associated with Equation 3.10 that need clarification, including the meanings of n and k, and the effect of the ion exchange capacity and the counter-ion concentration and/or charge. Inferences as to the nature of k were made in Chapter IV and it appeared to be related to the exchange capacity, but the form of the relationship is not clear at present. However, k does have modified concentration units (moles/liter to a fractional power). Consequently, this quantity has been treated as a proportionality constant, the magnitude of which depends upon the charge of the counter-ion.

The fractional exponent, n, of the co-ion A concentration has also been discussed previously. It too appears to be a constant, but dependent upon the counter-ion charge. For the limited data at hand, it seems possible empirically to separate the effect of charge as follows:

$$\bar{c}_B/c_B \;=\; kc_A^{\left[\frac{z_A^a}{z_X^x}\right] n'} \qquad\qquad (6.3)$$

This expression is limited to co-ions A and B of the same charge. Application of Equation 6.3 to the uni-univalent, uni-divalent, and di-univalent systems studied in this work yields values of n' all approximately 0.70. Conversion of the n's of Table 5.10 into (n')'s to conform to Equation 6.3 are shown in Table 6.5.

It may be seen that values of n' agree reasonably well for all of the systems. The average value of n' is 0.71, with a relative standard deviation of 12.7%. However, there is presently no rationale for including the ionic charges in the distribution expression and in the co-ion transport expression, and Equations 3.6 and 3.10 have been left as presented in Chapter III.

TABLE 6.5

EVALUATION OF n'

System	$c_{A,2}/c_{A,1}$	n	z_A^a/z_X^x	n'
^{22}NaCl-NaCl	1.0	0.75	1.0	0.75
^{22}NaCl-NaCl	0.1	0.71	1.0	0.71
^{137}CsCl-NaCl	1.0	0.76	1.0	0.76
^{137}CsCl-NaCl	0.1	0.78	1.0	0.78
^{137}CsCl-CsCl	1.0	0.79	1.0	0.79
^{137}CsCl-CsCl	0.1	0.81	1.0	0.81
^{22}Na$_2$SO$_4$-Na$_2$SO$_4$	1.0	0.19	0.25	0.76
^{22}Na$_2$SO$_4$-Na$_2$SO$_4$	0.1	0.15	0.25	0.60
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	1.0	0.16	0.25	0.64
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$	0.1	0.19	0.25	0.76
^{137}Cs$_2$SO$_4$-Cs$_2$SO$_4$	1.0	0.13	0.25	0.52
^{137}Cs$_2$SO$_4$-Cs$_2$SO$_4$	0.1	0.16	0.25	0.64
^{110m}AgNO$_3$-AgNO$_3$	1.0	0.68	1.0	0.68 *
^{133}BaCl$_2$-BaCl$_2$	1.0	>2	4	>0.5 *
Average				0.71

* These are not included in the average value of n'. The ^{110m}AgNO$_3$ - AgNO$_3$ system value of n' is unreliable (see Table 2.2) and the value for the ^{133}BaCl$_2$ - BaCl$_2$ system is an estimate of the lower limit of n'.

APPENDIX I

EXCHANGE EQUILIBRIUM THROUGH ANION EXCHANGE MEMBRANES
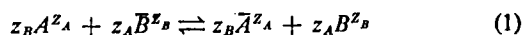
Exchange Equilibrium through Anion Exchange Membranes

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Previously developed theory for the cation distribution between two solutions separated by a cation exchange membrane at cation exchange equilibrium has been extended to and verified for the anion distribution through an anion exchange membrane. Some noticeable differences between the cation and anion exchange membranes are observed, particularly in the times required to reach exchange equilibrium. Also, the permselectivity of anion exchange membranes in systems containing divalent anions is much poorer than in systems containing univalent anions.

THE CATION EXCHANGE equilibrium between two solutions separated by a permselective cation exchange membrane has been recently described theoretically and experimentally, and possible analytical applications have been pointed out (*1*). This paper shows that the previously developed theory also describes the anion exchange equilibrium across an anion exchange membrane. In this study it is noticed that, for the particular anion exchange membranes and conditions used, the time to reach ion exchange equilibrium is considerably longer than that found for a comparable cation exchange membrane. Also, the permselectivity of anion exchange membranes in systems containing divalent anions is much poorer than in systems containing univalent anions. On account of these properties, anion exchange membranes may prove to be of more limited analytical use than cation exchange membranes.

Theory. The anion exchange equilibrium between two anionic species A and B, of charges z_A and z_B, respectively, may be represented by

$$z_B A^{z_A} + z_A \bar{B}^{z_B} \rightleftharpoons z_B \bar{A}^{z_A} + z_A B^{z_B} \tag{1}$$

where the barred quantities refer to the membrane phase. When two solutions (1 and 2) containing A and B are separated by an anion exchange membrane, the distribution of A and B at anion exchange equilibrium is described very simply by

$$\left(\frac{C_{A,1}}{C_{A,2}}\right)^{z_B/z_A} = \frac{C_{B,1}}{C_{B,2}} \tag{2}$$

This equation is derived directly from the well known Donnan Distribution Law and is only approximate, since molarities have been substituted for activities (*1*). In principle, Equation 2 should hold for A and B in all concentration ratios. However, if B is present only at trace levels, then at anion exchange equilibrium there is no significant change in the distribution of A from its initial distribution, and the concentration ratio initially selected for A sets the distribution of B at exchange equilibrium. The following experimental work was designed to verify Equation 2.

EXPERIMENTAL

Five different systems were studied in order to verify Equation 2 for anion exchange membranes. All contained a bulk electrolyte (the sodium salt of anion A), ranging in concentration from $0.0005M$ to $0.10M$, and a radiotracer
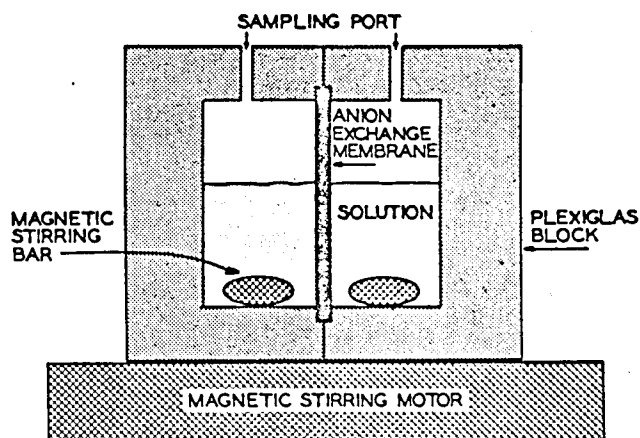
(1) W. J. Blaedel and T. J. Haupert, ANAL. CHEM., **38**, 1305 (1966).

Figure 1. Cell used for equilibrium distribution studies

(anion B). The five systems were: NaI with tracer ^{131}I as iodide, NaBr with tracer ^{125}I as iodide, NaCl with tracer ^{32}P as monohydrogen phosphate, Na$_2$HPO$_4$ with tracer ^{32}P as monohydrogen phosphate, and Na$_2$HPO$_4$ with tracer ^{125}I as iodide.

All chemicals were reagent grade, used without further purification. Radiotracers were carrier-free and diluted with water to appropriate activity levels. Because of the pH instability of pure Na$_2$HPO$_4$ solutions, these solutions were made up in $0.0001M$ NH$_4$Cl, the pH of which was adjusted to 9.0 by the addition of $2M$ NH$_3$.

Equilibrium distributions of the tracer between two solutions separated by the anion exchange membrane were measured to verify Equation 2 by a procedure similar to that used earlier (*1*). A 2.82 cm² piece of anion exchange membrane (AMF A-104-EB, American Machine and Foundry, Springdale, Conn., a graft polymer of polyethylene–polystyrene, having quaternary amine exchange groups) was placed between two blocks of Plexiglas (Rohm & Haas, Philadelphia, Pa.) in which identical 5.46-ml cavities were milled. Two such blocks, mirror images of each other, when bolted together, locked the membrane in place. Within each cavity was a half-inch Teflon-coated magnetic stirring bar. Two entrance ports were drilled into each piece of Plexiglas to facilitate sampling. The entire assembly was then mounted upon a magnetic stirring motor in order to obtain effective agitation of the solutions (Figure 1).

Before measuring the tracer distribution in each system, the anion exchange membrane was converted to the desired form by a 24-hour equilibration with $0.5M$ to $1.0M$ solution of the appropriate bulk electrolyte. Prior to the actual experiment, the cells were flushed twice with water and then filled with tracer-free solutions of the bulk electrolyte at the concentrations to be used later. With magnetic stirring, the membrane was allowed to equilibrate with these solutions for approximately 2 hours. The cells were then emptied, rinsed twice with portions of the solutions to be used in the experiments, drained, and excess solution blown out with a stream of nitrogen. Finally, 2.0 ml of the desired solutions were added to each compartment. At time zero, a small aliquot of radiotracer was added to the more concentrated solution (in a few cases the radiotracer was added to the more dilute solution) and stirring was begun.

The approach to anion exchange equilibrium was followed by withdrawing 50- or 100-μl aliquots from each compartment
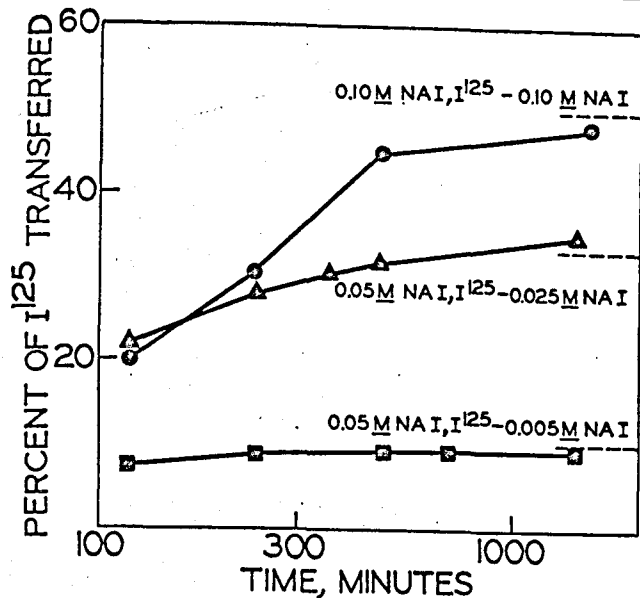
Figure 2. Time required for achievement of anion exchange equilibrium, NaI bulk electrolyte

Dashed horizontal lines indicate theoretical percent transport at equilibrium

at various times. These aliquots were diluted to a fixed volume (2.0 ml for ^{125}I, 0.5 ml for ^{32}P) and counted in polyethylene tubes (75 mm in length and 12 mm in diameter) to achieve a uniform counting geometry. The radioactivity of the aliquots was measured using a scintillation detector (Model 810c, Baird-Atomic, Cambridge, Mass.) along with a spectrometer (University II Series, Model 530, Baird-Atomic, Cambridge, Mass.). The counting intervals were adjusted to give at least 10,000 counts in order to minimize counting error.

Because of significant co-ion (cation) transport in some of the phosphate systems during the time required to reach anion exchange equilibrium, the bulk electrolyte concentrations of these systems did not remain at the initial values and it was necessary to assay the phosphate concentration chemically each time an aliquot was withdrawn from the cells. The method of Sumner (2) was used. Aliquots of the sample withdrawn for counting purposes were diluted with water to bring them within the proper concentration range for the phosphate determination, and 0.1-ml samples were taken. These aliquots were further diluted to 5.0 ml with water. To each sample was added 1.0 ml of 2.5% ammonium molybdate tetrahydrate in $5N$ H_2SO_4. After 10 minutes, 1.0 ml of 10% $FeSO_4$ was added, the solutions were mixed thoroughly, and 15 minutes were allowed for development of the molybdenum blue color. The absorbances of the solutions were measured colorimetrically at 660 mμ. The ratio of the absorbances from solutions on opposite sides of the membrane were taken as a measure of the tracer concentration ratio for that sample.

RESULTS AND DISCUSSION

Evaluation of Permselectivity for AMF A-104-EB Anion Exchange Membrane. The relative transport of tracer ^{137}Cs and of tracer ^{125}I through the anion exchange membrane separating two 0.01M NaI solutions is shown in Table I. It may be seen that over the first few hours, the amount of ^{125}I counter-ion transport is about 10^4 times greater than that of the ^{137}Cs co-ion transport. This also shows that anion ex-

(2) J. B. Sumner, *Science*, 100, 413 (1944).

Table I. Relative Transport of ^{125}I and ^{137}Cs through Anion Exchange Membranes

Time, hours	Transported, %	
	^{125}I counter-ion	^{137}Cs co-ion
1	27.5	0
2	39.0	0
4	45.3	0.002
8	47.8	0.008
24	48.4	0.032

Table II. Distribution of Counter-Ions at Anion Exchange Equilibrium in Uni-Univalent Bulk Electrolytes

Bulk electrolyte molarities (initial)		Equilibrium distributions		Difference % (col. 4 − col. 3)
$C_{A,1}$	$C_{A,2}$	Theoretical[a]	Experimental[b]	
Bulk electrolyte, NaBr ($z_A = 1$); tracer electrolyte, Na^{125}I ($z_B = 1$)				
0.10	0.10	1.0	0.98	−2.0
0.10	0.05	2.0	1.98	−1.0
0.10	0.025	4.0	3.99	−0.2
0.10	0.01	10.0	9.56	−4.2
0.10	0.005	20.0	18.08	−9.6
0.05	0.05	1.0	1.03	+3.0
0.05	0.025	2.0	2.08	+4.0
0.05	0.0125	4.0	3.78	−5.5
0.05	0.0125	4.0	4.06	+1.5
0.05	0.005	10.0	10.05	+0.5
0.05	0.0025	20.0	19.77	−1.2
0.01	0.01	1.0	1.06	+6.0
0.01	0.01	1.0	1.10	+10.0
0.01	0.005	2.0	2.10	+5.0
0.01	0.0025	4.0	3.90	−2.5
0.01	0.001	10.0	9.32	−6.8
0.01	0.0005	20.0	19.88	−0.6
Bulk electrolyte, NaCl ($z_A = 1$); tracer electrolyte, Na$_2$H^{32}PO$_4$ ($z_B = 2$)				
0.10	0.10	1.0	1.06	+6.0
0.10	0.10	1.0	1.00	0.0
0.10	0.05	4.0	4.11	+2.8
0.10	0.05	4.0	3.95	−1.2
0.10	0.033	9.0	9.52	+5.8
0.10	0.033	9.0	8.93	−0.8
0.10	0.025	16.0	15.55	−2.8
0.10	0.025	16.0	15.55	−2.8

[a] Initial concentration ratio of bulk electrolyte, $(C_{A,1}/C_{A,2})^{z_B/z_A}$.
[b] Measured tracer radioactivity ratio, $C_{B,1}/C_{B,2}$.

change equilibrium is reached within a few hours, during which time the co-ion distribution toward chemical equilibrium has barely begun to occur.

Verification of Counter-Ion Distribution According to Equation 2. In order to check the methods and techniques, 19 measurements (data not shown) of the equilibrium distribution of tracer ^{125}I were performed in systems with NaI bulk electrolyte concentrations ranging from 0.01M to 0.10M in solution 1 and from 0.0005M to 0.10M in solution 2. For all 19 experiments, the root mean square relative difference between the initial ratios of the bulk electrolyte concentrations in the two solutions (left side of Equation 2) and the tracer activity ratio (right side of Equation 2) was 4.2%. The median difference was +1.4%, indicating no systematic error. The r.m.s. relative difference of 4.2% represents experimental errors uncomplicated by neglect of activity coefficients, which cancel precisely in Equation 2 for ^{125}I–NaI systems.

Results for the equilibrium distributions of tracer ^{125}I in NaBr and tracer ^{32}P as monohydrogen phosphate in NaCl

Table III. Distribution of Counter-Ions at Anion Exchange Equilibrium in Na₂HPO₄ Systems

Bulk electrolyte molarities (initial)		Equilibrium distributions			Difference %
$C_{A,1}$	$C_{A,2}$	Theoretical[a] Initial	Measured	Experimental[b]	(col 5 − col 4)
Bulk electrolyte, Na₂HPO₄ ($z_A = 2$); tracer electrolyte, Na₂H³²PO₄ ($z_B = 2$)					
0.10	0.10	1.0	0.99	1.01	+2.0
0.10	0.10	1.0	0.99	1.02	+3.0
0.10	0.05	2.0	1.61	1.65	+2.5
0.10	0.025	4.0	2.69	2.57	−4.5
0.10	0.025	4.0	2.39	2.39	0.0
0.10	0.01	10.0	4.77	4.95	+4.6
0.10	0.01	10.0	4.03	4.23	+5.0
Bulk electrolyte, Na₂HPO₄ ($z_A = 2$); tracer electrolyte, Na¹²⁵I ($z_B = 1$)					
0.10	0.10	1.0	1.00	1.00	0.0
0.10	0.10	1.0	1.01	1.01	0.0
0.10	0.025	2.0	1.50	1.47	−2.0
0.10	0.025	2.0	1.58	1.54	−2.5
0.10	0.0111	3.0	1.83	1.78	−2.7
0.10	0.0111	3.0	1.99	1.98	−0.5
0.10	0.00625	4.0	2.11	2.08	−1.4
0.10	0.00625	4.0	2.19	2.11	−3.7

[a] Concentration ratio of bulk electrolyte, $(C_{A,1}/C_{A,2})^{z_B/z_A}$.
[b] Measured tracer radioactivity ratio, $C_{B,1}/C_{B,2}$.

are summarized in Table II. For the 25 experiments, the root mean square relative difference between the initial bulk electrolyte concentration ratio and the equilibrium radioactivity ratio is 4.4%. The median difference is −0.6%, indicating no systematic error. These data indicate the correctness of Equation 2 at the 4% error level, for uni- and divalent tracer types in uni-univalent bulk electrolyte concentrations ranging from 0.0005M to 0.10M.

Figure 2 shows times required to reach anion exchange equilibrium in three typical systems. These times are several-fold longer than the time for cation exchange equilibrium to occur in comparable systems (1).

For the equilibrium distribution of ¹²⁵I in Na₂HPO₄ and of ³²P as monohydrogen phosphate in Na₂HPO₄ the results

were not so straightforward. At the concentration levels used, there was considerable transport of the bulk electrolyte through the membrane. This phenomenon was observed only when using a bulk electrolyte containing divalent mono-hydrogen phosphate anions. Consequently, the initial concentration ratios were always high when compared to the tracer activity ratios, as was done in Table II. However, when chemical measurements of the bulk monohydrogen phosphate electrolyte were made on the aliquots withdrawn for counting, it was found that the actual chemical concentration ratios, at anion exchange equilibrium, were indeed in good agreement with the tracer radioactivity ratios. The data are shown in Table III. The root mean square relative difference between the measured concentration ratios (column 4) and the radio-tracer ratios (column 5) for 15 experiments is 2.8%. The median difference is 0.0%, indicating no systematic error.

Table IV. Transport of ¹³⁷Cs Co-Ions through Anion Exchange Membranes in NaI and Na₂SO₄ Systems

Bulk electrolyte molarities (initial)		Tracer transferred
$C_{A,1}$	$C_{A,2}$	at 24 hours, %
Bulk electrolyte, NaI ($z_A = 1$)		
0.10	0.10	0.05
0.10	0.05	0.13
0.10	0.025	0.16
0.10	0.01	0.17
0.10	0.005	0.09
0.05	0.05	0.12
0.05	0.025	0.03
0.05	0.0125	0.07
0.05	0.005	0.05
0.05	0.0025	0.07
0.01	0.01	0.03
0.01	0.005	0.06
0.01	0.0025	0.09
0.01	0.001	0.01
0.01	0.0005	0.04
Bulk electrolyte, Na₂SO₄ ($z_A = 2$)		
0.10	0.10	8.4
0.10	0.025	8.7
0.10	0.0111	7.1
0.10	0.00625	7.6
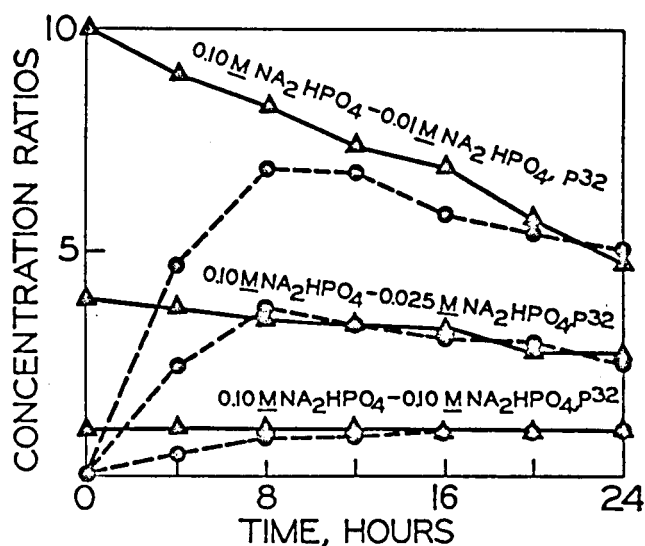
Figure 3. Time required for achievement of anion exchange equilibrium, Na₂HPO₄ bulk electrolyte

Solid lines represent measured concentration ratios, while dashed lines represent tracer concentration ratios

The data of Table III extend verification of Equation 2 to systems with bulk electrolytes having divalent anions.

Figure 3 shows the extent of the transport of the bulk electrolyte as a function of time for the self-diffusion system of ^{32}P as monohydrogen phosphate in Na_2HPO_4. In these experiments, the radiotracer was placed initially in the more dilute solution. It is apparent that transport of the bulk electrolyte in the Na_2HPO_4 system occurs much more rapidly than in the uni-univalent NaI system of Figure 2, but that the chemical and tracer concentration ratios still approach each other in accord with Equation 2.

Co-Ion Transport. In order to determine whether the increased amount of co-ion transport in the uni-divalent Na_2HPO_4 system was a charge effect or chemically specific, the transport of co-ion tracer ^{137}Cs was compared in NaI and Na_2SO_4 solutions, with the results shown in Table IV. While the ionic strength of the Na_2SO_4 solutions is somewhat greater than that of the NaI solutions, the amount of co-ion transport of ^{137}Cs is about two orders of magnitude greater when the divalent anion is present as compared to a univalent anion. Apparently, the anionic charge of the bulk electrolyte greatly influences the amount of co-ion transport through anion exchange membranes. The data in Table IV also indicate that the extent of co-ion transport is independent of the bulk electrolyte concentration ($C_{A,2}$) of solution 2 and only slightly dependent upon the bulk electrolyte concentration ($C_{A,1}$) of solution 1. All of these effects cannot be explained quantitatively by Donnan Exclusion.

It was established that the great co-ion transport in divalent anionic systems was not accompanied by great changes in pH or water movement. At present, explanations of the dependence of co-ion transport upon counter-ion charge type are highly speculative, and so are explanations of the highly different transport rates of counter-ions through anion and cation exchange membranes. An extended study is under way to establish theoretically and experimentally the factors upon which the rates of counter-ion and co-ion transport depend.

ACKNOWLEDGMENT

APPENDIX II

OTHER DISTRIBUTION EXPRESSIONS AND TRANSPORT EQUATIONS

Prior to the development of the co-ion transport theory presented in Chapter III, two other distributions of the co-ion between the solution and membrane phases were postulated; one based on a simple Freundlich Adsorption Isotherm for co-ion B alone, and one postulating the presence of small amounts of cation exchanger in the anion exchange membrane. The distribution expressions and the resulting co-ion transport equations obtained are given below.

SIMPLE FREUNDLICH ADSORPTION ISOTHERM FOR CO-ION B ALONE

Distribution Expression

$$\overline{C}_B = kC_B^{\ n} \tag{II.1}$$

Transport Equation

$$\frac{C_{B,1}^{\ n}}{C_{B,2}} = \frac{V_2\overline{L}}{At\overline{D}_Bk} \tag{II.2}$$

Equation II.2 was not used because the tracer ratio is independent of the bulk co-ion A concentration, contrary to experimental observations.

LOW CAPACITY CATION EXCHANGER PRESENT IN THE ANION EXCHANGE MEMBRANE

The postulated cation exchange reaction was

$$B + n\bar{A} \rightleftharpoons \bar{B} + nA \qquad (II.3)$$

Distribution Expression

$$\bar{C}_B = \frac{K\bar{C}_A{}^n C_B}{C_A{}^n} \qquad (II.4)$$

In Equation II.4, K is the equilibrium distribution constant.

Transport Equation

$$\frac{C_{B,1}}{C_{B,2}} = \frac{V_2 \bar{L} C_{A,1}{}^n}{At\bar{D}_B K Q^n} + \left[\frac{C_{A,1}}{C_{A,2}}\right]^n \qquad (II.5)$$

Q is the ion exchange capacity of the membrane. Equation II.5 states that the tracer ratio is directly proportional to $(C_{A,1})^n$, instead of inversely proportional, as was experimentally observed.

APPENDIX III

RAW DATA AND CALCULATIONS FOR TYPICAL CO-ION DISTRIBUTION MEASUREMENTS

The procedure for carrying out distribution measurements of co-ion B between solution and membrane phases was given in Chapter IV. Examples of the raw data obtained in these studies are given here for the distribution of ^{137}CsCl in CsCl at bulk electrolyte concentrations of 0.10 $\underline{M}$ and 0.01 $\underline{M}$, and for ^{137}Cs$_2$SO$_4$ in Cs$_2$SO$_4$ at bulk electrolyte concentrations of 0.20 $\underline{M}$ and 0.02 $\underline{M}$. Each determination was made in duplicate. The calculations are outlined below for Sample A1 from the ^{137}CsCl-CsCl system (p. 45), and are summarized in the accompanying table.

OUTLINE OF CALCULATIONS FOR SAMPLE A1 (^{137}CsCl–CsCl)

1. Calculate the membrane volume ($\overline{V}$, col. 14) from the membrane weight ($\overline{w}$, col. 12) and membrane density ($\overline{\rho}$, col. 13), known from Chapter II.

$$\overline{V} \;=\; \frac{\overline{w}}{\overline{\rho}}$$

$$=\; \frac{0.0304}{0.999} \;=\; 0.0304 \text{ ml}$$

2. Convert sample c/5m (cols. 3, 6, 7, 8) to corrected c/5m (cols. 5, 10) by subtracting the background bk/5m (cols. 4, 9).

3. Calculate solution phase c/m/ml (col. 15).

$$\text{Solution phase c/m/ml} \;=\; \frac{\text{Solution phase c/5m (col. 5)}}{5 \times 0.10 \text{ ml}}$$

$$=\; \frac{156383}{5 \times 0.10} \;=\; 312766 \text{ c/m/ml}$$

4. Calculate membrane phase c/m/ml (col. 16).

$$\text{Membrane phase c/m/ml} = \frac{\text{Membrane phase c/5m (col. 10)}}{5 \times \overline{V} \text{ (col. 14)}}$$

$$= \frac{233}{5 \times 0.0304} = 1533 \text{ c/m/ml}$$

5. Calculate $\overline{C}_B/C_B$ (col. 17).

$$\overline{C}_B/C_B = \frac{\text{Membrane phase c/m/ml (col. 16)}}{\text{Solution phase c/m/ml (col. 15)}}$$

$$= \frac{1533}{312766} = 0.00490$$

Sample	C_A	Solution Phase			Membrane Phase				
		c/5m	bk/5m	cc/5m	c/5m	c/5m	c/5m	bk/5m	acc/5m
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
				^{137}CsCl–CsCl					
A1	0.100	156474	91	156383	328	320	328	96	233
A2	0.100	93565	91	93474	215	268	252	96	149
E1	0.010	102403	91	102312	115	105	117	96	16
E2	0.010	96969	91	96878	134	126	137	96	36
				^{137}Cs$_2$SO$_4$–Cs$_2$SO$_4$					
A1	0.200	113350	254	113096	766	733	733	86	658
A2	0.200	105720	254	105446	723	683	672	86	608
E1	0.020	113261	254	113007	482	501	475	86	400
E2	0.020	118193	254	117939	510	478	482	86	404

LEGEND: c/5m = counts/5 minutes, bk/5m = background counts/5m, cc/5m = corrected counts/5m, acc/5m = average corrected counts/5m.

Sample (11)	$\bar{w}$, g (12)	$\bar{\rho}$, g/ml (13)	$\bar{V}$, ml (14)	Solution c/m/ml (15)	Membrane c/m/ml (16)	$\bar{C}_B/C_B$ (17)	Average $\bar{C}_B/C_B$ (18)
^{137}CsCl–CsCl							
A1	0.0304	0.999	0.0304	312766	1533	0.00490	0.00496
A2	0.0317	0.999	0.0317	186948	940	0.00503	
E1	0.0273	0.999	0.0273	204624	117	0.00057	0.00084
E2	0.0335	0.999	0.0335	193756	215	0.00110	
^{137}Cs$_2$SO$_4$–Cs$_2$SO$_4$							
A1	0.0268	1.040	0.0258	226192	5116	0.0226	0.0257
A2	0.0207	1.040	0.0199	210892	6080	0.0288	
E1	0.0207	1.040	0.0199	226014	4017	0.0178	0.0177
E2	0.0203	1.040	0.0195	235878	4147	0.0176	

LEGEND: $\bar{w}$ = membrane weight, $\bar{\rho}$ = membrane density, $\bar{V}$ = membrane volume, c/m/ml = counts/minute/ml.

APPENDIX IV

RAW DATA FOR TYPICAL CO-ION TRANSPORT MEASUREMENTS

The procedure used to measure co-ion transport from Solution 1 to Solution 2 through an ion exchange membrane was given in Chapter V. Examples of the raw data for the co-ion transport for ^{137}CsCl in NaCl bulk electrolyte at concentrations of 0.10 $\underline{M}$ and 0.01 $\underline{M}$, and for ^{137}Cs$_2$SO$_4$ in Na$_2$SO$_4$ bulk electrolyte at concentrations of 0.20 $\underline{M}$ and 0.02 $\underline{M}$ are given in the following table, with determinations made in quadruplicate at each concentration level. In all cases, the bulk co-ion A concentration was the same on both sides of the membrane. The evaluation of the tracer ratio, $C_{B,1}/C_{B,2}$, at 24 hours was made by dividing the Solution 1 counts per 5 minutes by the Solution 2 counts per 5 minutes. The legend for the abbreviations used in column headings may be found on p. 108.

EXAMPLES OF TRANSPORT STUDY DATA

Sample	$C_{A,1}$ $\underline{M}$	Time, hrs	Solution 1			Solution 2					$C_{B,1}/C_{B,2}$
			c/5m	bk/5m	cc/5m	c/5m	c/5m	c/5m	bk/5m	acc/5m	
					^{137}CsCl–NaCl						
A1	0.100	24	70206	49	70157	608	597	583	36	560	125
B1	0.100	24	68431	49	68382	546	506	499	36	481	142
C1	0.100	24	68486	49	68437	581	607	574	36	551	124
D1	0.100	24	70495	49	70446	578	624	582	36	559	126
A5	0.010	24	41014	48	40966	77	92	81	30	53	773
B5	0.010	24	40722	48	40674	77	91	91	30	56	726
C5	0.010	24	41619	48	41529	85	90	88	30	58	716
D5	0.010	24	40927	48	40879	99	78	100	30	62	659
					^{137}Cs$_2$SO$_4$–Na$_2$SO$_4$						
A1	0.200	24	66543	40	66503	2664	2599	2536	30	2569	25.9
B1	0.200	24	65212	40	65172	2685	2649	2671	30	2638	24.7
C1	0.200	24	66292	40	66252	2702	2675	2785	30	2691	24.7
D1	0.200	24	66444	40	66404	3114	3044	3082	30	3050	21.8
A5	0.020	24	41541	40	41501	1239	1294	1221	38	1213	34.2
B5	0.020	24	40564	40	40524	1259	1217	1257	38	1203	33.5
C5	0.020	24	41278	40	41238	1237	1242	1276	38	1213	34.0
D5	0.020	24	41059	40	41019	1329	1387	1377	38	1326	32.9

APPENDIX V

CO-ION STUDIES WITH OTHER ANION EXCHANGE MEMBRANES

APPENDIX V

CO-ION STUDIES WITH OTHER ANION EXCHANGE MEMBRANES

The theory describing the transport of a radiotracer co-ion B

from one solution to another through an ion exchange membrane was

developed in Chapter III of this thesis. Subsequent chapters have

dealt with the experimental evaluation and interpretation of the

theory. All experimental work presented thus far was done using

the AMF A-104-EB anion exchange membrane. In this appendix, repe-

tition of some of the previous studies is presented using two addit-

ional anion exchangers.

MEMBRANE CHARACTERISTICS

The anion permselective membranes, CA-1 (concentration anion)

and DA-1 (desalinization anion), are manufactured by the Asahi Chemical

Industry Company, Limited, Tokyo, Japan. They are prepared by a pro-

cess different from that used by AMF. Essentially, styrene, divinyl-

benzene, and other materials are copolymerized into a solid block.

Thin sheets of the plastic are planed off, and then subjected to the

chloromethylation and amination reactions necessary to introduce the

quaternary ammonium anion exchange groups. It should be noted that

this procedure yields a more homogeneous membrane as compared to the

AMF species, because there is no inert supporting material present

such as polyethylene.

According to the manufacturer's specifications (32), the CA-1 membrane has an ion exchange capacity of 2.0 meq/g dry resin, a thickness of 0.023 cm, and a water content of 31%, while the DA-1 membrane has a capacity of 1.6 meq/g dry resin, a thickness of 0.023 cm, and a water content of 26%. From work done in this study (see Chapter II for the procedures), it was found that the CA-1 membrane has an ion exchange capacity of 1.219 meq/cm^3 of wet resin, and the DA-1 species has a capacity of 0.912 meq/cm^3 of wet resin. Wet thickness of the membranes, measured by the pyncometric technique earlier described, are 0.0211 cm for the CA-1 membrane and 0.0202 cm for the DA-1 membrane (membrane densities are 1.118g/cm^3 and 1.105g/cm^3, respectively). These membrane parameters compare with literature values of capacity - 1.30 meq/g wet membrane, water content - 31.3%, and wet thickness - 0.019 cm (10). The values of the experimentally determined membrane properties for the CA-1, DA-1, and A-104-EB membranes are summarized in Table V.1 for purposes of comparison.

One additional characteristic of the Asahi membranes must be noted. Experimentally, it was found that these membranes are very brittle and easily crack upon handling and cutting. Therefore, extreme care must be used when working with them.

TABLE V.1

CHARACTERISTICS OF THE CA-1, DA-1, AND A-104-EB ANION EXCHANGE MEMBRANES

Parameter	CA-1	DA-1	A-104-EB
Capacity, meq/cm^3 wet membrane	1.219	0.912	1.048
Water content, %*	31	26	20
Density, g/cm^3	1.118	1.105	1.020
Thickness, wet, cm	0.0211	0.0202	0.0153

* Manufacturer's specification

DISTRIBUTION STUDIES

Co-ion distribution studies similar to those described in Chapter IV were made on the CA-1 and DA-1 membranes using the $^{137}CsCl-NaCl$ and $^{137}Cs_2SO_4-Na_2SO_4$ systems. The data are presented in Table V.2 along with comparison values for the A-104-EB membrane. As is observed, the values of n for the Asahi membranes are quite similar to those found for the AMF membrane, while k is significantly higher than previously observed.

TRANSPORT STUDIES

A series of co-ion transport studies were carried out on the CA-1 and DA-1 membranes to investigate the effect of $C_{A,1}$ on the tracer ratio, $C_{B,1}/C_{B,2}$. The techniques described in Chapter V were used, except that no stirring of the external solutions was employed due to the fragile nature of the Asahi membranes. The $^{137}CsCl-NaCl$ and $^{137}Cs_2SO_4-Na_2SO_4$ systems were used in this work. In all cases, the concentration of co-ion A was the same on each side of the membrane.

Table V.3 shows the data obtained for the CA-1 and DA-1 membranes, as well as that obtained previously for the A-104-EB species. All values are the means of quadruplicate determinations made 24 hours after the initiation of the experiments. The median relative standard deviation is around 5.0%. It is noted that the value of the tracer ratio for both types of Asahi membranes is much lower than those pre-

TABLE V.2

EVALUATION OF n AND k FROM DISTRIBUTION STUDIES

	n			k	
CA-1	DA-1	A-104-EB	CA-1	DA-1	A-104-EB
^{137}CsCl-NaCl					
0.77	0.84	0.77	0.083	0.12	0.024
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$					
0.15	0.13	0.16	0.11	0.11	0.037

TABLE V.3

DEPENDENCE OF THE CO-ION TRANSPORT ON $C_{A,1}$

$C_{A,1}$, $\underline{M}$	$(C_{B,1}/C_{B,2}) - 1$		
	CA-1	DA-1	A-104-EB
^{137}CsCl-NaCl			
0.100	11.1	4.13	128
0.075	13.0	5.22	144
0.050	17.4	7.34	216
0.025	30.2	13.3	353
0.010	67.4	31.4	717
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$			
0.200	2.53	1.22	21.7
0.150	2.35	1.23	22.6
0.100	2.47	1.26	24.3
0.050	2.59	1.38	26.0
0.020	3.39	1.82	32.2

viously found, showing that co-ion transport is much faster.

Table V.4 gives the values of n for each system obtained by a least squares analysis of a log-log plot of $(C_{B,1}/C_{B,2}) - 1$ versus $C_{A,1}$, as well as the relative standard deviations. Values of n and their standard deviations are about the same for the Asahi and AMF membranes.

SUMMARY

Inspection of the data for the CA-1 and DA-1 membranes shows certain interesting points. First, the value of the exponent n for a given counter-ion system is essentially the same for all the membranes studied. Second, the proportionality constant, k, is significantly larger for both Asahi membranes as compared to the AMF species. The fundamental significance of these similarities and differences, if any, is not understood at this time.

On the other hand, the amount of transport of tracer co-ion B through the membrane in 24 hours is much higher for both of the Asahi membranes, and consequently, the value of the ordinate intercept from the log-log plot of $(C_{B,1}/C_{B,2}) - 1$ versus $C_{A,1}$ is much lower. Table V.5 shows the values of the intercepts and their relative standard deviations for all three membranes studied. Also listed are values of the co-ion membrane diffusion coefficients, calculated as described in Chapter VI.

TABLE V.4

EVALUATION OF n FROM TRANSPORT STUDIES

n			Relative Standard Deviation, %		
CA-1	DA-1	A-104-EB	CA-1	DA-1	A-104-EB
^{137}CsCl-NaCl					
0.79	0.88	0.76	2.8	1.2	3.9
^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$					
0.14	0.17	0.16	25.9	16.3	10.6

TABLE V.5

EVALUATION OF $\bar{D}_B$

Parameter	Membrane		
	CA-1	DA-1	A-104-EB
	^{137}CsCl-NaCl		
Ordinate Intercept	1.70	0.58	21.6
Relative Standard Deviation, %	6.5	2.6	5.3
k	0.083	0.12	0.024
$\bar{D}_B \times 10^7$, cm^2/sec	10.6	20.1	2.42
	^{137}Cs$_2$SO$_4$-Na$_2$SO$_4$		
Ordinate Intercept	1.70	0.78	15.6
Relative Standard Deviation, %	6.8	5.7	6.9
k	0.11	0.11	0.037
$\bar{D}_B \times 10^7$, cm^2/sec	8.24	16.1	2.17

It is immediately noticed that the values of $\overline{D}_B$ for co-ions in the two Asahi membranes are much larger than those found for the AMF membrane. This increase in the value of the membrane diffusion coefficient for the trace co-ion B is consistent with the higher rate of co-ion transport through the CA-1 and DA-1 membranes. A partial explanation for the high value of $\overline{D}_B$ in the Asahi membrane is that they do not have the inert polyethylene supporting material that the A-104-EB membrane does, and as a result, a much greater amount of the membrane volume is available for ionic diffusion.

In summary, the Asahi membranes, by virtue of their preparation, contain only ion exchanger material, whereas the AMF membrane is only partially ion exchanger. However, the permselectivity of the AMF membrane is about an order of magnitude greater than that found for the CA-1 and DA-1 species. It appears that the co-ion transport theory presented in this thesis can be applied to several different types of ion exchange membranes with good results.

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